

PCT

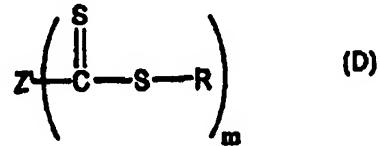
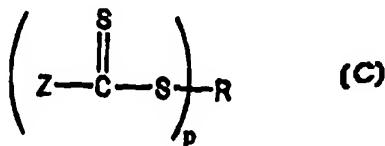
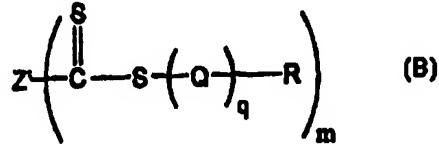
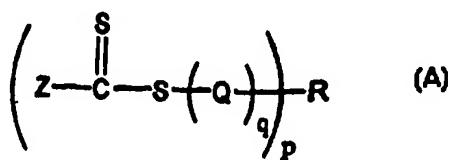
WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

CA

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08F 2/38, C07C 327/36		A1	(11) International Publication Number: <b>WO 98/01478</b> (43) International Publication Date: 15 January 1998 (15.01.98)
(21) International Application Number: PCT/US97/12540 (22) International Filing Date: 3 July 1997 (03.07.97)		(81) Designated States: AU, BR, CA, CN, IL, JP, KR, MX, NZ, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(30) Priority Data: PO 0933 10 July 1996 (10.07.96) AU PO 1109 18 July 1996 (18.07.96) AU		Published With International search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).			
(72) Inventors; and (73) Inventors/Applicants (for US only): LE, Tam, Phuong [AU/AU]; 18 Quist Court, Mill Park, VIC 3082 (AU). MOAD, Graeme [AU/AU]; Bellamay 137, Monbulk Road, Kallista, VIC 3791 (AU). RIZZARDO, Ezio [AU/AU]; 26 Alex Avenue, Wheelers Hill, VIC 3150 (AU). THANG, San, Hoa [AU/AU]; 180 Clarinda Road, Clayton South, VIC 3169 (AU).			
(74) Agent: COSTELLO, James, A.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).			

(54) Title: POLYMERIZATION WITH LIVING CHARACTERISTICS



## (57) Abstract

This invention concerns a free radical polymerization process, selected chain transfer agents employed in the process and polymers made thereby, in which the process comprises preparing polymer of general Formula (A) and Formula (B) comprising contacting: (i) a monomer selected from the group consisting of vinyl monomers (of structure  $\text{CH}_2 - \text{CUV}$ ), maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers; (ii) a thiocarbonylthio compound selected from Formula (C) and Formula (D) having a chain transfer constant greater than about 0.1; and (iii) free radicals produced from a free radical source; the polymer of Formula (A) being made by contacting (i), (ii) C and (iii) and that of Formula (B) by contacting (i), (ii) D, and (iii); and (iv) controlling the polydispersity of the polymer being formed by varying the ratio of the number of molecules of (ii) to the number of molecules of (iii); wherein Q, R, U, V, Z, Z', m, p and q are as defined in the text.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

TITLE

## POLYMERIZATION WITH LIVING CHARACTERISTICS

BACKGROUND OF THE INVENTION

5

This invention relates to a free radical polymerization process with characteristics of a living polymerization system in that it is capable of producing polymers of pre-determined molecular weight with narrow molecular weight distribution (low polydispersity), and, by successively adding different monomers.

10 can be used to make block polymers. The process can be used to produce polymers of more complex architecture, including variously branched homo- and copolymers. The use of certain reagents in this process and the polymers produced thereby are also claimed. Novel chain transfer agents for use in the process are also claimed.

15 There is increasing interest in methods for producing a variety of polymers with control of the major variables affecting polymer properties. Living polymerizations provide the maximum degree of control for the synthesis of polymers with predictable well defined structures. The characteristics of a living polymerization are discussed by Quirk and Lee (*Polymer International* 27, 359 20 (1992)) who give the following experimentally observable criteria:

- 25 1. Polymerization proceeds until all of the monomer has been consumed. Further addition of monomer results in continued polymerization.
2. The number average molecular weight (or the number average degree of polymerization) is a linear function of conversion.
3. The number of polymer molecules (and active centers) is a constant which is sensibly independent of conversion.
4. The molecular weight can be controlled by the stoichiometry of the reaction.
- 30 5. Narrow molecular weight distribution polymers are produced.
6. Block copolymers can be prepared by sequential monomer addition.
7. Chain end-functionalized polymers can be prepared in quantitative yield. "

35

Living polymerization processes can be used to produce polymers of narrow molecular weight distribution containing one or more monomer sequences whose length and composition are controlled by the stoichiometry of the reaction

and the degree of conversion. Homopolymers, random copolymers or block polymers can be produced with a high degree of control and with low polydispersity. Swarc (*Adv. Polym. Sci.* **49**, 1 (1983)) stated that living polymerization to give polymers of narrow molecular weight distribution requires

5 the absence of chain transfer and termination reactions, the elementary reactions being only initiation and propagation, which take place uniformly with respect to all growing polymer chains. Later Inoue and Aida in an article on living polymer systems (*Encyclopedia of Polymer Science and Engineering, Supplement Volume*, Wiley Interscience New York 1989) stated "If chain transfer and

10 terminating agents are present in the polymerization system the living character of the polymerization is lost, and the formation of polymer with narrow molecular weight distribution does not result."

However, it has been shown that if the chain transfer process is reversible then polymerization can still possess most of the characteristics of living

15 polymerization. A variety of terms have been used to describe polymerizations believed to involve this mechanism including "immortal polymerization", "equilibration polymerization", "polymerization with degenerative chain transfer" and "living polymerization with reversible chain transfer". Quirk and Lee (*Polymer International* **27**, 359 (1992)), who recommend the last terminology,

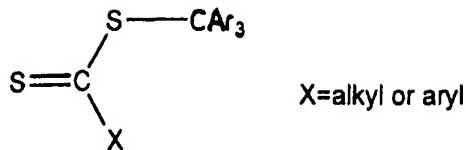
20 point out that the Criteria 3 and 4 mentioned above need to be modified when describing these polymerizations to encompass the fact that the total number of polymer molecules is determined by the total number of moles of transfer agent plus the number of moles of initiator.

Block copolymer syntheses by free radical polymerization in the presence

25 of certain dithiocarbamate or xanthate derivatives as initiator-transfer agents-chain terminators (iniferters) have been described. In these examples the dithiocarbamate or xanthate derivative is used as a photochemical initiator. For a discussion of this chemistry see recent reviews [Moad *et al.* in *Comprehensive Polymer Science*; Pergamon: London, vol 3, p 141 (1989)]. The dithiocarbamates

30 (for example, benzyl dithiocarbamate) have very low transfer constants (<<0.1) and are ineffective in the context of the current invention. Greszta *et al.* (*Macromolecules*, **27**, 638 (1994)) have described the application of chain transfer chemistry in living radical polymerization and have proposed and rejected the use of dithiocarbamates in this context because of the low transfer constant and the

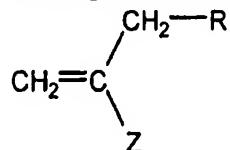
35 problem of side reactions. JP 04198303 A2 discloses polymerization in the presence of triaryl methyl dithiocarboxylates of the following structure



as initiators of polymerization to yield block polymers which may have low polydispersity (all examples have  $M_w/M_n > 1.4$ ). These compounds have a very weak carbon-sulfur bond that cleaves under polymerization conditions to give a

5 stable triarylmethyl radical and a thiocarbonylthiyl radical. The product  
triarylmethyl radical is known to be a poor initiator of radical polymerization.  
They are thus ineffective in the context of this invention.  
Rizzardo *et al.* (*Macromol. Symp.* **98**, 101 (1995)) review polymerization in the  
presence of addition-fragmentation chain transfer agents but do not mention the  
0 possibility of low polydispersity products.

Polymers or oligomers of the following structure are known as macromonomers.

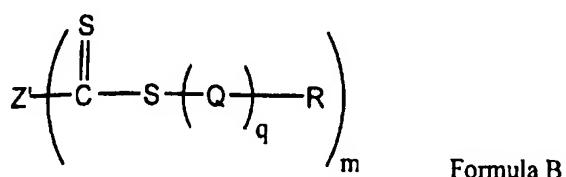
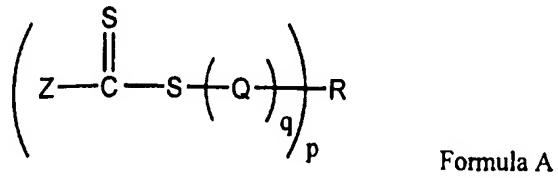


These macromonomers which are addition-fragmentation chain transfer agents are disclosed in *J Macromol. Sci. - Chem.* **A23**, 839 (1986) and

15 International Patent publications WO 93/22351 and WO 93/22355. Free radical polymerization with living characteristics utilizing these macromonomers as chain transfer agents is disclosed in International Patent Application PCT/US95/14428. The process of this invention has the advantages of compatibility with a wide range of monomers and reaction conditions and will give good control over 20 molecular weight, molecular weight distribution, i.e., polydispersity, and polymer architecture.

## SUMMARY OF THE INVENTION

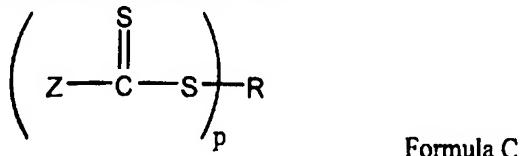
This invention concerns a process for the synthesis of polymers of the general Formula:



comprising contacting:

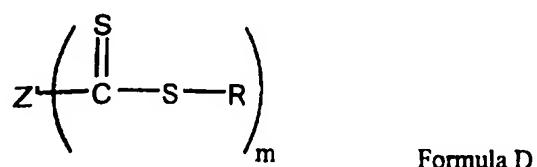
10

- (i) a monomer (means one or more) selected from the group consisting of vinyl monomers (of structure  $\text{CH}_2=\text{CUV}$ ), maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers;
- 15 (ii) a thiocarbonylthio compound selected from:



and

20



having a chain transfer constant greater than about 0.1; and

25 (iii) free radicals produced from a free radical source; and

controlling the polydispersity of the polymer being formed by varying the ratio of the number of molecules of (ii) to the number of molecules of (iii);

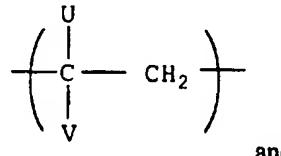
the polymer of Formula A being made by contacting (i), (ii)C and (iii) and the 5 polymer of Formula B being made by contacting (i), (ii) D and (iii);

wherein:

Z is selected from the group consisting of hydrogen, chlorine, optionally 10 substituted alkyl, optionally substituted aryl, optionally substituted heterocycll, optionally substituted alkylthio, optionally substituted alkoxy carbonyl, optionally substituted aryloxy carbonyl (-COOR"), carboxy (-COOH), optionally substituted acyloxy (-O<sub>2</sub>CR"), optionally substituted carbamoyl (-CONR"2), cyano (-CN), dialkyl- or diaryl- phosphonato [-P(=O)OR"2], dialkyl- or diaryl-phosphinato 15 [-P(=O)R"2], and a polymer chain formed by any mechanism;

Z' is a m-valent moiety derived from a member of the group consisting of 20 optionally substituted alkyl, optionally substituted aryl and a polymer chain; where the connecting moieties are selected from the group that consists of aliphatic carbon, aromatic carbon, and sulfur;

Q is selected from the group consisting of



and

repeating units from maleic anhydride, N-alkylmaleimide, N-arylmaleimide, 25 dialkyl fumarate and cyclopolymerizable monomers;

U is selected from the group consisting of hydrogen, halogen, optionally substituted C<sub>1</sub>-C<sub>4</sub> alkyl wherein the substituents are independently selected from the group that consists of hydroxy, alkoxy, aryloxy (OR"), carboxy, acyloxy, 30 aroyloxy (O<sub>2</sub>CR"), alkoxy- carbonyl and aryloxy-carbonyl (CO<sub>2</sub>R");

V is selected from the group consisting of hydrogen, R", CO<sub>2</sub>H, CO<sub>2</sub>R", COR", CN, CONH<sub>2</sub>, CONHR", CONR"2, O<sub>2</sub>CR", OR" and halogen;

R is selected from the group consisting of optionally substituted alkyl; an optionally substituted saturated, unsaturated or aromatic carbocyclic or heterocyclic ring; optionally substituted alkylthio; optionally substituted alkoxy; optionally substituted dialkylamino; an organometallic species; and a polymer  
5 chain prepared by any polymerization mechanism; in compounds C and D, R<sup>•</sup> is a free-radical leaving group that initiates free radical polymerization;

R" is selected from the group consisting of optionally substituted C<sub>1</sub>-C<sub>18</sub> alkyl, C<sub>2</sub>-C<sub>18</sub> alkenyl, aryl, heterocycl, aralkyl, alkaryl wherein the substituents  
10 are independently selected from the group that consists of epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy (and salts), sulfonic acid (and salts), alkoxy- or aryloxy-carbonyl, isocyanato, cyano, silyl, halo, and dialkylamino;

15 q is 1 or an integer greater than 1;  
p is 1 or an integer greater than 1; when p≥2, then R=R';

m is an integer ≥2; and  
20 R' is a p-valent moiety derived from a member of the group consisting of optionally substituted alkyl, optionally substituted aryl and a polymer chain; where the connecting moieties are selected from the group consisting of aliphatic carbon, aromatic carbon, silicon, and sulfur; in compounds C and D, R'<sup>•</sup> is a free radical leaving group that initiates free radical polymerization.  
25

Preferred is a process as described for controlling polydispersity by varying the ratio of the number of molecules of (ii) to (iii) as follows:  
30 (a) lower polydispersity by increasing the ratio of (ii) to (iii); and  
(b) increase polydispersity by decreasing the ratio of (ii) to (iii).

Most preferred is the process in which the ratio of (ii) to (iii) is increased to obtain a polymer having a polydispersity below about 1.5.

35 The monomer moieties and value of q in the monomer repeating unit(s) derived from those in (i) are selected so that:  
when q ≥1 and Q is a single monomer species, then the polymer is homopolymer;

when  $q \geq 2$  and Q is selected from 2 or more different monomer species in irregular sequence then the polymer is copolymer; and

when  $q \geq 2$  and Q is selected from 2 or more different monomer species in which each different monomer or group of monomers appears in a discrete sequence then

5 the polymer is block copolymer.

The invention also concerns chain transfer agents designated hereafter as (5), (6), (7), (8), (9), (10), (11), (14), (15), (17), (18), (19), (22), (23), (24), (25), (28) and (29). The invention also concerns polymers of Formulae A and B with

10 substituents as defined above. In polymers of Formulae A and B, R $\bullet$  and R' $\bullet$  are derived from free radical leaving group(s) that initiate free radical polymerization, R-(Q) $q\bullet$  and R'-(Q) $q\bullet$  being the free radical leaving group(s) that initiate free radical polymerization. Preferred polymers are random, block (most preferred), graft, star and gradient copolymers; most especially those having chain-end

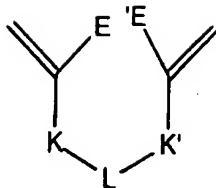
15 functionality. Compounds of Formulae C and D can be used to produce branched, homo- or copolymers with the number of arms being less than or equal to p in C and m in D.

#### Definitions

20 By polymer chains formed by any mechanism (in Z or R), is meant: condensation polymers such as polyesters (for example, polycaprolactone, polyethylene terephthalate), polycarbonates, poly(alkylene oxide)s [for example, poly(ethylene oxide), poly(tetramethylene oxide)], nylons, polyurethanes and chain polymers such as poly(meth)acrylates and polystyrenics.

25 Cyclopolymerizable monomers are compounds which contain two or more unsaturated linkages suitably disposed to allow propagation by a sequence of intramolecular and intermolecular addition steps leading to the incorporation of cyclic units into the polymer backbone. Most compounds of this class are 1,6-dienes such as - diallylammonium salts (e.g., diallyldimethylammonium chloride),

30 substituted 1,6-heptadienes (e.g., 6-dicyano-1,6-heptadiene, 2,4,4,6-tetrakis(ethoxycarbonyl)-1,6-heptadiene) and monomers of the following generic structure



where substituents K, K', L, E, E' are chosen such that the monomer undergoes cyclopolymerization. For example:

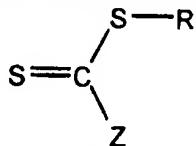
5

E, E' are independently selected from the group consisting of H, CH<sub>3</sub>, CN, CO<sub>2</sub>Alkyl, Ph; K, K' are selected from the group consisting of CH<sub>2</sub>, C=O, Si(CH<sub>3</sub>)<sub>2</sub>, O; L is selected from the group consisting of C(E)<sub>2</sub>, O, N(Alkyl)<sub>2</sub> salts, P(Alkyl)<sub>2</sub> salts, P(O)Alkyl. For a further list of monomers see Moad and  
10 Solomon "The Chemistry of Free Radical Polymerization", Pergamon, London, 1995, pp 162-170.

By organometallic species is meant a moiety containing one or more metal atoms from Groups III and IV of the Periodic Table and transition elements and  
15 organic ligands, preferably species such as Si(X)<sub>3</sub>, Ge(X)<sub>3</sub> and Sn(X)<sub>3</sub> which can be good radical leaving groups and initiate polymerization.

#### DETAILS OF THE INVENTION

We have now discovered that free radical polymerizations when carried  
20 out in the presence of certain chain transfer agents of the following structure:



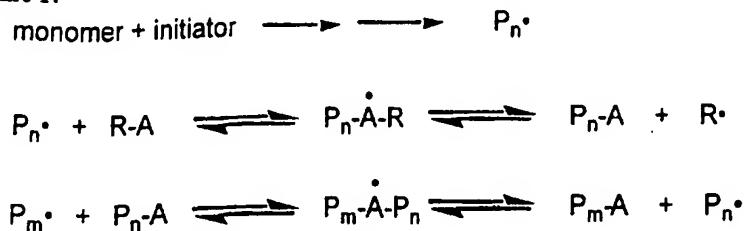
have living characteristics and provide polymers of controlled molecular weight and low polydispersity. Chain transfer agents applicable in this invention are designated as CTAs hereinafter.

25 While not wishing to be limited to any particular mechanism, it is believed that the mechanism of the process is as summarized in Scheme 1 below. Propagating radicals P<sub>n</sub>• are produced by radical polymerization. These can react reversibly with the chain transfer agent RA to form an intermediate radical P<sub>n</sub>A(•)R which fragments to give a radical R• (which adds monomer to reinitiate  
30 polymerization) and a new transfer agent P<sub>n</sub>A. This new transfer agent P<sub>n</sub>A has similar characteristics to the original transfer agent RA in that it reacts with

another propagating radical  $P_m\cdot$  to form an intermediate radical  $P_nA(\cdot)P_m$  which fragments to regenerate  $P_n\cdot$  and form a new transfer agent  $P_mA$  which has similar characteristics to RA. This process provides a mechanism for chain equilibration and accounts for the polymerization having living characteristics.

5

**Scheme 1:**



$P_n\cdot$  and  $P_m\cdot$  are propagating radicals of chain length n and m respectively.

10  $R\cdot$  is a chain transfer agent derived radical which can initiate polymerization to produce a new propagating radical.  
RA,  $P_nA$  and  $P_mA$  are CTAs.

This invention provides a free radical polymerization process with living  
15 characteristics which process comprises polymerizing one or more free radically polymerizable monomers in the presence of a source of initiating free radicals and a chain transfer agent (CTA) of Formula C or D which CTA during the polymerization reacts with the initiating or propagating radicals to give both a new radical that initiates further polymerization and a polymeric CTA also of  
20 Formula C or D (where R is the former initiating or propagating radical) with similar characteristics to the original CTA, the reaction conditions being chosen so that the ratio of the total number of initiator-derived radicals to the number of CTA molecules is maintained at a minimum value consistent with achieving an acceptable rate of polymerization, preferably less than 0.1, and the chain transfer  
25 constants of the CTAs are greater than 0.1, preferably greater than 1, and more preferably, greater than 10.

Initiating radicals are free radicals that are derived from the initiator or other species which add monomer to produce propagating radicals. Propagating radicals are radical species that have added one or more monomer units and are  
30 capable of adding further monomer units.

All of the benefits which derive from the use of radical polymerization can now be realized in syntheses of low polydispersity homo- and copolymers. The ability to synthesize block, graft, star, gradient and end-functional polymers

further extends the value of the process as does compatibility with protic monomers and solvents.

The source of initiating radicals can be any suitable method of generating free radicals such as the thermally induced homolytic scission of a suitable compound(s) (thermal initiators such as peroxides, peroxyesters, or azo compounds), the spontaneous generation from monomer (e.g., styrene), redox initiating systems, photochemical initiating systems or high energy radiation such as electron beam, X- or gamma-radiation. The initiating system is chosen such that under the reaction conditions there is no substantial adverse interaction of the initiator or the initiating radicals with the transfer agent under the conditions of the experiment. The initiator should also have the requisite solubility in the reaction medium or monomer mixture.

Thermal initiators are chosen to have an appropriate half life at the temperature of polymerization. These initiators can include one or more of the following compounds:

2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-cyano-2-butane), dimethyl 2,2'-azobisdimethylisobutyrate, 4,4'-azobis(4-cyanopentanoic acid), 1,1'-azobis(cyclohexanecarbonitrile), 2-(t-butylazo)-2-cyanopropane, 2,2'-azobis[2-methyl-N-(1,1)-bis(hydroxymethyl)-2-hydroxyethyl] propionamide, 2,2'-azobis[2-methyl-N-hydroxyethyl]-propionamide, 2,2'-azobis(N,N'-dimethyleneisobutyramidine) dihydrochloride, 2,2'-azobis(2-amidinopropane) dihydrochloride, 2,2'-azobis(N,N'-dimethyleneisobutyramine), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl] propionamide), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl) ethyl] propionamide), 2,2'-azobis[2-methyl-N-(2-hydroxyethyl) propionamide], 2,2'-azobis(isobutyramide) dihydrate, 2,2'-azobis(2,2,4-trimethylpentane), 2,2'-azobis(2-methylpropane), t-butyl peroxyacetate, t-butyl peroxybenzoate, t-butyl peroxyoctoate, t-butyl peroxyneodecanoate, t-butyl peroxy isobutyrate, t-amyl peroxyvalate, t-butyl peroxyvalate, di-isopropyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, dicumyl peroxide, dibenzoyl peroxide, dilauroyl peroxide, potassium peroxydisulfate, ammonium peroxydisulfate, di-t-butyl hyponitrite, dicumyl hyponitrite.

35

Photochemical initiator systems are chosen to have the requisite solubility in the reaction medium or monomer mixture and have an appropriate quantum yield for radical production under the conditions of the polymerization. Examples

include benzoin derivatives, benzophenone, acyl phosphine oxides, and photo-redox systems.

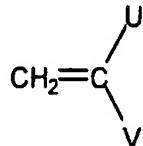
Redox initiator systems are chosen to have the requisite solubility in the reaction medium or monomer mixture and have an appropriate rate of radical 5 production under the conditions of the polymerization; these initiating systems can include combinations of the following oxidants and reductants:

oxidants: potassium peroxydisulfate, hydrogen peroxide, t-butyl hydroperoxide.

10 reductants: iron (II), titanium (III), potassium thiosulfite, potassium bisulfite.

Other suitable initiating systems are described in recent texts. See, for example, Moad and Solomon "The Chemistry of Free Radical Polymerization", 15 Pergamon, London, 1995, pp 53-95.

The process of the invention can be applied to any monomers or monomer combinations which are susceptible to free-radical polymerization. Such monomers include those with the general structure:

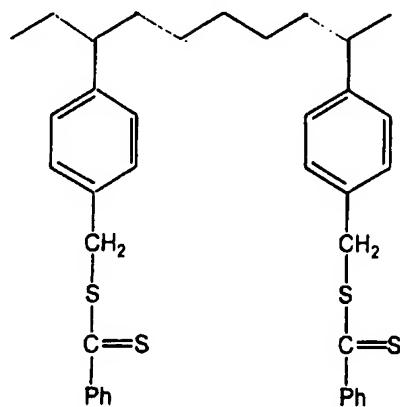


where U and V are as defined above. Optionally, the monomers are selected from the group that consists of maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers. Monomers CH<sub>2</sub>=CUV as 25 used herein include acrylate and methacrylate esters, acrylic and methacrylic acid, styrene, acrylamide, methacrylamide, and methacrylonitrile, mixtures of these monomers, and mixtures of these monomers with other monomers. As one skilled in the art would recognize, the choice of comonomers is determined by their steric and electronic properties. The factors which determine copolymerizability of 30 various monomers are well documented in the art. For example, see: Greenley, R.Z. in *Polymer Handbook* 3rd Edition (Brandup, J., and Immergut, E.H. Eds.) Wiley: New York, 1989 p II/53.

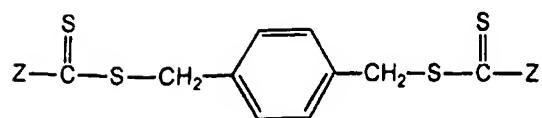
Specific monomers or comonomers include the following:

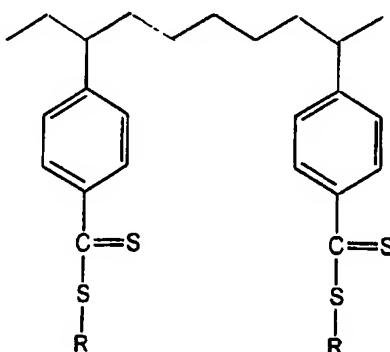
35 methyl methacrylate, ethyl methacrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), 2-ethylhexyl methacrylate, isobornyl methacrylate,

methacrylic acid, benzyl methacrylate, phenyl methacrylate, methacrylonitrile,  
alpha-methylstyrene, methyl acrylate, ethyl acrylate, propyl acrylate (all isomers),  
butyl acrylate (all isomers), 2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid,  
benzyl acrylate, phenyl acrylate, acrylonitrile, styrene, functional methacrylates,  
5 acrylates and styrenes selected from glycidyl methacrylate, 2-hydroxyethyl  
methacrylate, hydroxypropyl methacrylate (all isomers), hydroxybutyl  
methacrylate (all isomers), N,N-dimethylaminoethyl methacrylate, N,N-  
diethylaminoethyl methacrylate, triethyleneglycol methacrylate, itaconic  
anhydride, itaconic acid, glycidyl acrylate, 2-hydroxyethyl acrylate,  
10 hydroxypropyl acrylate (all isomers), hydroxybutyl acrylate (all isomers), N,N-  
dimethylaminoethyl acrylate, N,N-diethylaminoethyl acrylate, triethyleneglycol  
acrylate, methacrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-tert-  
butylmethacrylamide, N-n-butylmethacrylamide, N-methylolmethacrylamide, N-  
ethylolmethacrylamide, N-tert-butylacrylamide, N-n-butylacrylamide, N-  
15 methylolacrylamide, N-ethylolacrylamide, vinyl benzoic acid (all isomers),  
diethylaminostyrene (all isomers), alpha-methylvinyl benzoic acid (all isomers),  
diethylamino alpha-methylstyrene (all isomers), p-vinylbenzene sulfonic acid, p-  
vinylbenzene sulfonic sodium salt, trimethoxysilylpropyl methacrylate,  
triethoxysilylpropyl methacrylate, tributoxysilylpropyl methacrylate,  
20 dimethoxymethylsilylpropyl methacrylate, diethoxymethyl-  
silylpropylmethacrylate, dibutoxymethylsilylpropyl methacrylate,  
diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate,  
diethoxysilylpropyl methacrylate, dibutoxysilylpropyl methacrylate,  
diisopropoxysilylpropyl methacrylate, trimethoxysilylpropyl acrylate,  
25 triethoxysilylpropyl acrylate, tributoxysilylpropyl acrylate,  
dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate,  
dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate,  
dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl  
acrylate, diisopropoxysilylpropyl acrylate, vinyl acetate, vinyl butyrate, vinyl  
30 benzoate, vinyl chloride, vinyl fluoride, vinyl bromide, maleic anhydride, N-  
phenylmaleimide, N-butylmaleimide, N-vinylpyrrolidone, N-vinylcarbazole,  
butadiene, isoprene, chloroprene, ethylene, propylene.

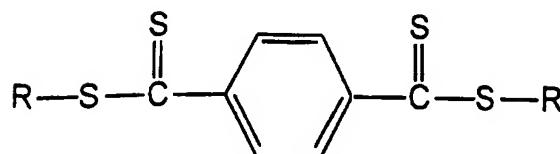
Examples of multifunctional ( $p \geq 2$ ) structures represented by Formula C

5



Examples of multifunctional ( $m \geq 2$ ) structures represented by Formula D

5



Many such structures are possible of which the following compounds are illustrative. Additional structures are found in the Examples section.  
 In the compounds of Formulae C and D substituted rings can have reactive  
 10 substituent groups directly or indirectly attached to the ring by means of a  
 15 methylene group or other side chain.

The substituents on groups referred to above for R, R', R", Z, Z' in  
 Formulae A-D and U, V, R" in the monomer do not take part in the  
 polymerization reactions but form part of the terminal groups of the polymer  
 15 chains and may be capable of subsequent chemical reaction. The low  
 polydispersity polymer containing any such reactive group is thereby able to  
 undergo further chemical transformation, such as being joined with another  
 polymer chain. Suitable reactive substituents include: epoxy, hydroxy, alkoxy,  
 acyl, acyloxy, carboxy (and salts), sulfonic acid (and salts), alkylcarbonyloxy,  
 20 isocyanato, cyano, silyl, halo, and dialkylamino. Alternatively, the substituents  
 may be non-reactive such as alkoxy, alkyl or aryl. Reactive groups should be  
 chosen such that there is no adverse reaction with the CTA under the conditions of  
 the experiment. For example, groups such as primary or secondary amino -NH<sub>2</sub>, -  
 NHalkyl) under some conditions may react with dithioesters to give thioamides  
 25 thus destroying the CTA.

Unless specified otherwise alkyl groups referred to in this specification  
 may be branched or unbranched and contain from 1 to 18 carbon atoms. Alkenyl  
 groups may be branched or unbranched and contain from 2 to 18 carbon atoms.

Saturated, unsaturated, or aromatic carbocyclic or heterocyclic rings may contain from 3 to 14 atoms.

"Heterocyclic" or "heterocycl" means a ring structure containing 3 to

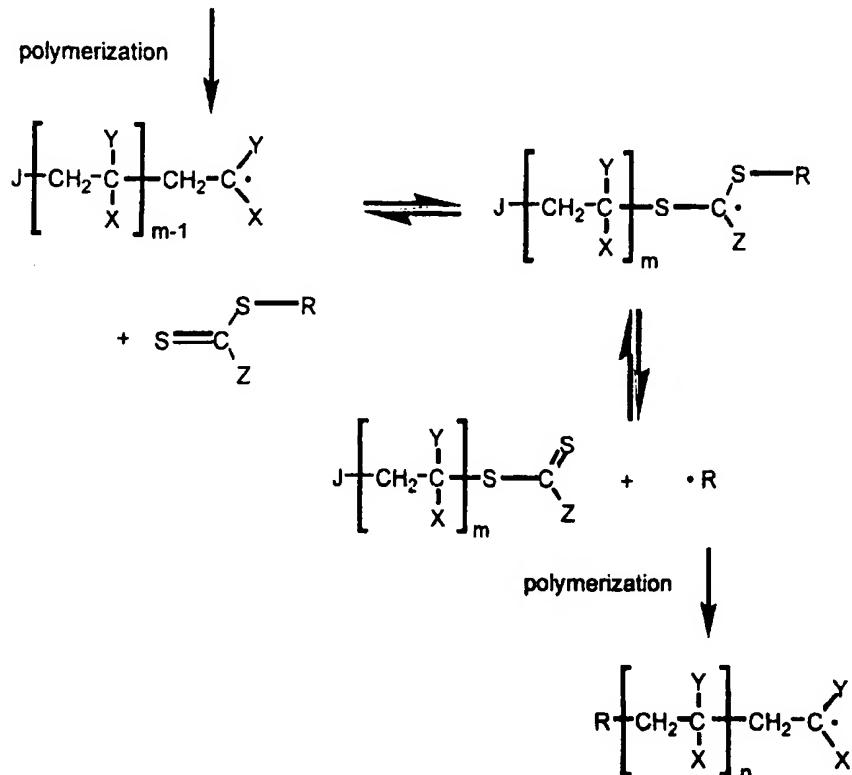
10 atoms at least one of which is selected from O, N and S, which may or

5 may not be aromatic. Examples of aromatic "heterocycl" moieties are pyridyl, furanyl, thienyl, piperidinyl, pyrrolidinyl, pyrazoyl, benzthiazolyl, indolyl, benzofuranyl, benzothiophenyl, pyrazinyl, quinolyl, and the like, optionally substituted with one or more alkyl, haloalkyl, halo, nitro, or cyano groups. "Ph" means phenyl.

10 An example of the preferred class of CTAs are the dithioesters (Formula C, p=1) such as are depicted in Scheme 2 which is illustrative of the reaction mechanism believed to be operative in the process of this invention. It should be understood, however, that the invention is not limited to the mechanism depicted and that other mechanisms may be involved.

15

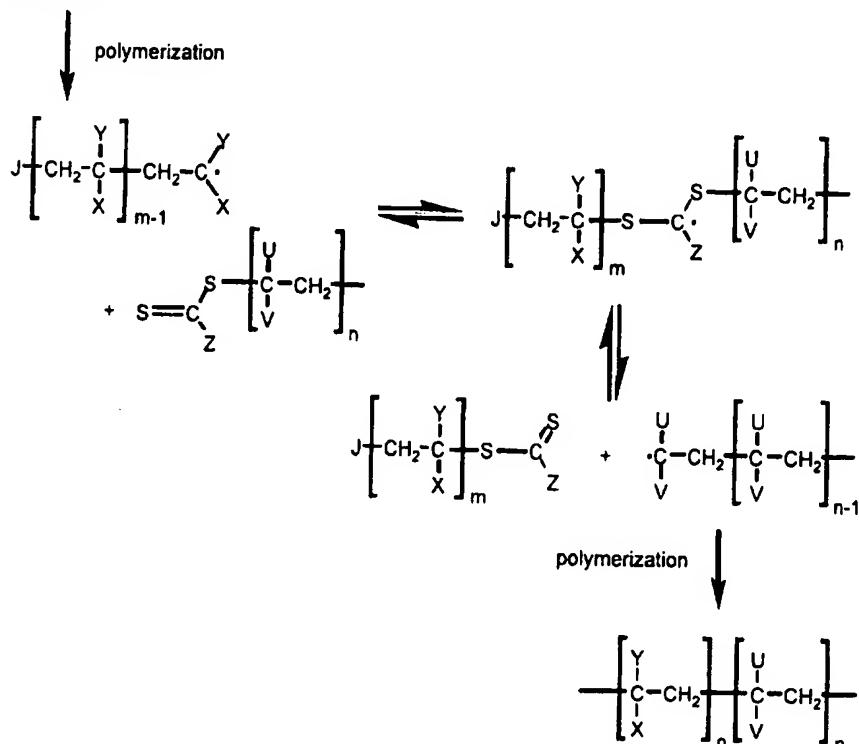
**Scheme 2:**



J is a fragment derived from an initiating or propagating radical.

A key feature of the invention is the retention of the active thiocarbonylthio end group[-C(S)-S-] in the polymeric product. The invention thus also provides a route to block polymers as illustrated, for example, in Scheme 3.

**Scheme 3:**



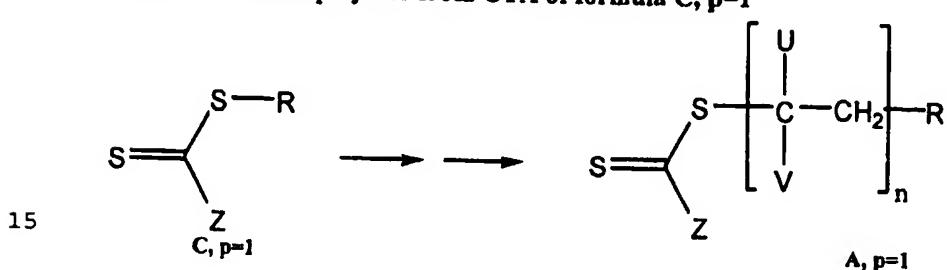
5

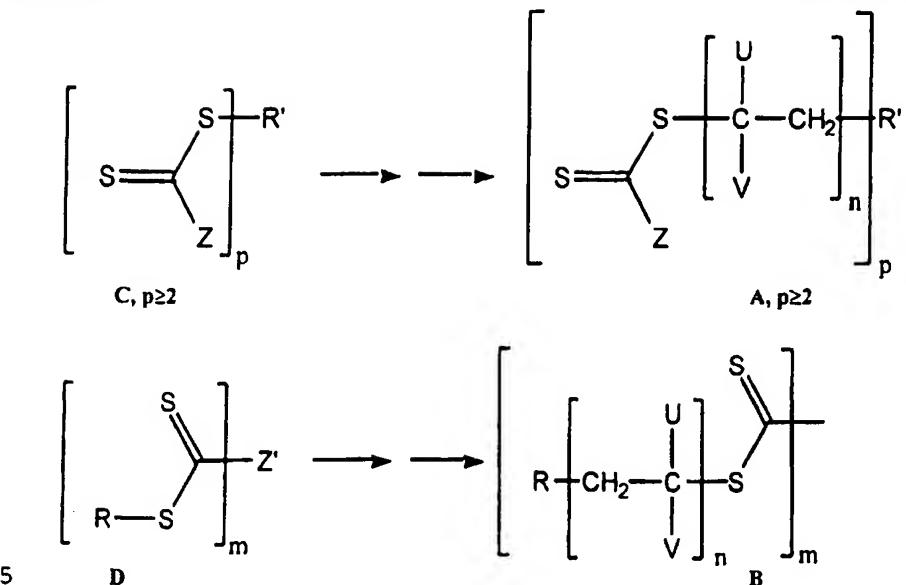
J is a fragment derived from an initiating or a propagating radical.

10 Polymers with complex architectures including multiblock, branched, star and graft polymers are available through the use of reagents containing multiple thiocarbonylthio groups as indicated by formulae C (where  $p \geq 2$ ) and D. The overall process is shown in Scheme 4

**Scheme 4:**

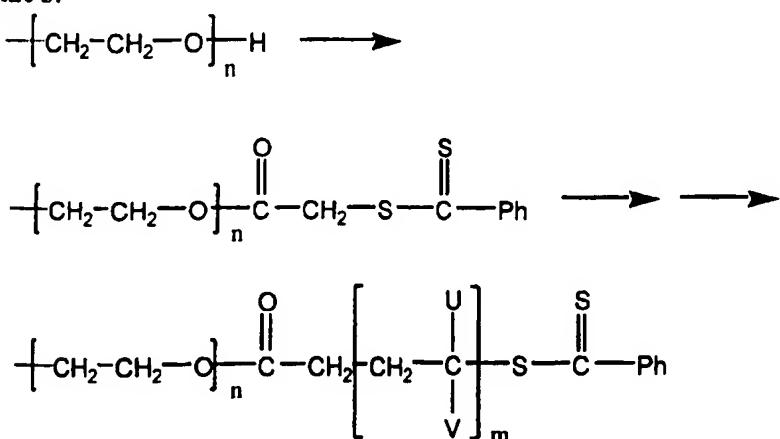
## Formation of linear polymer from CTA of formula C<sub>n</sub>-1





Block, star or graft polymers can be formed from polymers (prepared by any polymerization mechanism) that contain the thiocarbonylthio [-S-C(=S)-] linkage. Methods for forming dithoester and related groups are well-documented in the art. The following example (Scheme 5) of forming a block copolymer from poly(ethylene oxide) is illustrative of the process.

**Scheme 5:**



15

Benefits of the polymerization process described in this invention are:

a) Low polydispersity polymers can be synthesized.

In the context of the present invention, low polydispersity polymers are those with polydispersities that are significantly less than those produced by conventional free radical polymerization. In conventional free radical polymerization, polydispersities (the 5 polydispersity is defined as the ratio of the weight average and number average molecular weights -  $M_w/M_n$ ) of the polymers formed are typically in the range 1.6-2.0 for low conversions (<10%) and are substantially greater than this for higher conversions. Polydispersities obtained with the 10 present invention are usually less than 1.5, often less than 1.3 and, with appropriate choice of the chain transfer agent and the reaction conditions, may be less than 1.1. The low polydispersity can be maintained at high conversions (see Examples).

Note that it is also possible to produce polymers with broad, yet 15 controlled, polydispersity or multimodal molecular weight distribution by controlled addition of the CTA over the course of the polymerization process.

Müller et al. have derived relationships which enable 20 polydispersities to be estimated for polymerizations which involve chain equilibration by reversible chain transfer (Müller, A.H.E.; Zhuang, R.; Yan, D.; Litvenko, G. *Macromolecules*, 1995, 28, 4326)

$$M_w/M_n = 1 + 1/C_{tr}$$

This above relationship should apply to batch polymerizations 25 carried to full conversion in the situation where the number of initiator-radical derived chains is small with respect to total chains and there are no side reactions.

This relationship suggests that the transfer constant should be > 2 to obtain a polydispersity < 1.5 in a batch polymerization. If the transfer 30 constant is < 2, low polydispersities (<1.5) may still be obtained in feed polymerization processes by choosing an appropriate monomer to transfer agent ratio and continuing the polymerization for a sufficient period to produce the desired molecular weight and polydispersity. In these circumstances, kinetic simulation can be used to aid in selecting reaction 35 conditions.

In theory, it is possible to use reagents with very low transfer constants (<0.1). However, in this case it is likely that side reactions will complicate the polymerization process. In practice, polydispersities are

likely to be higher than predicted by these relationships because of the limitations already mentioned. Nonetheless, these relationships serve as a useful guide in selecting reaction conditions.

5 b) Molecular weights increase in a predictable and linear manner with conversion (see Examples) which is controlled by the stoichiometry. In the case of monofunctional CTAs of Formulae C and D the molecular weight of the product can be calculated according to the relationship:

$$10 \quad \text{MW}_{\text{prod}} = \frac{[\text{moles monomer consumed}]}{[\text{moles CTA}]} \times \text{MW}_{\text{mon}} + \text{MW}_{\text{cta}}$$

Where:  $MW_{prod}$  is the number average molecular weight of the isolated polymer

$MW_{mon}$  is the molecular weight of the monomer

$MW_{cta}$  is the molecular weight of the CTA of formula C or D.

15 This expression applies under reaction conditions where the number of initiator-derived chains is small with respect to total chains.

Note that this form of molecular weight control is very different to that seen in free radical polymerization in the presence of conventional transfer agents.

20 agents.

c) The process can be used to provide various low polydispersity polymers including:

- End-functional polymers
- Block and multiblock and gradient polymers
- Star polymers
- Graft or branched polymers.

30 d) The process of this invention is compatible with a wider range of monomers and reaction conditions than other processes for producing low polydispersity and reactive polymers. Specific advantages of the present process are:

35 i) The much higher transfer constant of compounds of Formula C or D (transfer constant can be  $>20$ ) in comparison to macromonomers (transfer constant  $<2$ ) means that it is not necessary to use starved-feed conditions to obtain low polydispersity polymers or block polymers. It is possible to use a batch polymerization process (see Examples).

ii) The compounds of Formula C or D do not undergo copolymerization with monomers. Therefore, low polydispersity polymers based on monosubstituted monomers (e.g., acrylic monomers, styrene) can be carried out under a wider range of reaction conditions.

5

The choice of the CTA compound is important in synthesis of low polydispersity polymers. The preferred dithioesters and related compounds give chain transfer with high chain transfer constants.

The transfer constant is defined as the ratio of the rate constant for chain transfer to the rate constant for propagation at zero conversion of monomer and CTA compound. If chain transfer occurs by addition-fragmentation, the rate constant for chain transfer ( $k_{tr}$ ) is defined as follows:

$$k_{tr} = k_{add} \times \frac{k_{\beta}}{k_{-add} + k_{\beta}}$$

where  $k_{add}$  is the rate constant for addition to the CTA and  $k_{-add}$  and  $k_{\beta}$  are the rate constants for fragmentation in the reverse and forward directions respectively. Based on the addition-fragmentation mechanism, four factors can be seen to influence the effectiveness of the CTA in the process of this invention:

- a) The rate of reaction of the CTA ( $RA$  and  $AP_n$  in Scheme 1).
- b) The partitioning of the intermediate radicals ( $P_nA^*R$  and  $P_nA^*P_m$  in Scheme 1) between starting materials and products.
- c) The rate of fragmentation of the intermediate radicals ( $P_nA^*R$  and  $P_nA^*P_m$  in Scheme 1).
- d) The ability of the expelled radicals ( $R^*$  and  $P_n^*$  in Scheme 1) to reinitiate polymerization. Factors a) and b) determine the magnitude of the transfer constant of the CTA compound.

Preferably, the transfer constant for the addition-fragmentation chain transfer process is  $>0.1$ . The polydispersity obtained under a given set of reaction conditions is sensitive to the value of the transfer constant. Lower polydispersities will result from the use of reagents with higher transfer constants. Benzyl dithiobenzoate derivatives have transfer constants which are estimated to be  $>20$  in polymerization of styrene or acrylate esters. Higher transfer constants also allow greater flexibility in the choice of reaction conditions. For reagents with low chain transfer constants, the use of feed addition is advantageous to obtain low polydispersities.

The chain transfer activity of CTAs of Formula C or D is a function of the substituents R and Z and the particular propagating radical. R should be chosen

so as to be a free radical leaving group under the polymerization conditions (and yet retain ability to reinitiate polymerization - see below). In styrene polymerization, dithiobenzoate CTAs (RA in Scheme 1) where A is PhCS<sub>2</sub>- and R is -C(Me)<sub>2</sub>Ph, -C(Me)<sub>2</sub>CN, -C(Me)<sub>2</sub>CO<sub>2</sub>Alkyl, -C(Me)<sub>2</sub>CH<sub>2</sub>C(Me)<sub>3</sub>, -C(Me)<sub>3</sub>, -C(Me)HPh, -CH<sub>2</sub>Ph, -CH<sub>2</sub>CO<sub>2</sub>H are all effective in giving narrowed polydispersity and molecular weight control under batch polymerization conditions (see Examples). On the other hand, in MMA polymerization, effectiveness decreases in the order where R is: -C(Me)<sub>2</sub>Ph<sup>3</sup> > -C(Me)<sub>2</sub>CN > -C(Me)<sub>2</sub>CO<sub>2</sub>Alkyl > -C(Me)<sub>2</sub>CH<sub>2</sub>C(Me)<sub>3</sub>, -C(Me)<sub>3</sub> > -C(Me)HPh > -CH<sub>2</sub>Ph. Of these reagents, only those dithiobenzoates where R = -C(Me)<sub>2</sub>Ph or -C(Me)<sub>2</sub>CN are effective in giving both narrowed polydispersity and molecular weight control under batch polymerization conditions. The dithiobenzoate where R = -C(Me)<sub>2</sub>CO<sub>2</sub>Et provides good molecular weight control but broader polydispersity. These results can be related to the magnitude of the transfer constant for the CTA and to the free radical leaving group ability of the R substituent with respect to that of the propagating radical. For example, the dithiobenzoates with R = -C(Me)HPh and -CH<sub>2</sub>Ph, which are ineffective in providing living characteristics to the batch polymerization of MMA at 60°C, have transfer constants of 0.15 and 0.03 respectively. These R groups are poor free radical leaving groups with respect to the MMA propagating radical.

It is also important to bear these considerations in mind in block copolymer synthesis. For example, the polystyryl propagating species (-P<sub>n</sub> = -[CH<sub>2</sub>-CHPh]<sub>n</sub> in Scheme 1) is a poorer free radical leaving group than the poly(methyl methacrylate) propagating species (-P<sub>n</sub> = -[CH<sub>2</sub>-C(Me)(CO<sub>2</sub>Me)]<sub>n</sub> in Scheme 1). Thus, for synthesis of poly(methyl methacrylate-*block*-styrene) under batch polymerization conditions the poly(methyl methacrylate) block is made first in order to make a narrow polydispersity block copolymer.

If the reaction is carried out under conditions whereby the monomer is fed to maintain a lower monomer to CTA ratio, reagents with lower transfer constants can be used successfully. Thus, a polystyrene polymeric CTA has been successfully converted to poly(methyl methacrylate-*block*-styrene) under feed polymerization conditions.

Z in formulae **C** and **D** should be chosen to give a high reactivity of the double bond towards addition (while not slowing the rate of fragmentation to the extent that there is an unacceptable retardation of polymerization - see below). For example, the transfer constant increases in the series where Z = -NMe<sub>2</sub> < -OMe < -SMe < -Me < -Ph. The compound Z = NEt<sub>2</sub>, R = CH<sub>2</sub>Ph has a very low transfer constant (<0.01) and is ineffective in polymerizations of styrene and

methyl methacrylate and vinyl acetate. Xanthate esters ( $Z = -O\text{-alkyl}$ ) also have low transfer constants in polymerizations of styrene and methyl methacrylate (0.1) and are not effective in imparting living characteristics to polymerizations of these monomers. These compounds are not part of the present invention.

5 On the other hand, dithioccompounds with  $Z = -S\text{-alkyl}$ ,  $-\text{alkyl}$  or  $-\text{aryl}$  (and other substituents as defined herein) have high transfer constants (the compound  $Z = \text{Ph}$ ,  $R = \text{CH}_2\text{Ph}$  has a transfer constant of  $>20$  in styrene polymerization at  $60^\circ\text{C}$ ) and are effective.

10 Factors c) and d), as set out above, determine whether or not there is retardation of polymerization and the extent of any retardation. If the overall rate of reinitiation is greater than or equal to the rate of propagation there will be no retardation. These factors will be influenced by the substituents R and Z in formulae C and D and the nature of the propagating radical.

15 We have also found that the relative rates of addition and of fragmentation can be estimated using molecular orbital calculations (For details of the method see Moad, G., Moad, C.L., Rizzardo, E., and Thang, S.H., *Macromolecules*, 1996, 29, 7717). This method and information on radical reactivities (see for example Moad and Solomon "The Chemistry of Free Radical Polymerization", Pergamon, London, 1995), when taken together with the information provided herein, will 20 assist those skilled in the art in selecting transfer agents for particular polymerizations.

25 For heterogeneous polymerization, it is desirable to choose a CTA which has appropriate solubility parameters. For aqueous emulsion polymerization, the CTA should preferably partition in favour of the organic (monomer) phase and yet have sufficient aqueous solubility that it is able to distribute between the monomer droplet phase and the polymerization locus.

30 The choice of polymerization conditions is also important. The reaction temperature will influence the rate parameters discussed above. For example, higher reaction temperatures will typically increase the rate of fragmentation. 35 Conditions should be chosen such that the number of chains formed from initiator-derived radicals is minimized to an extent consistent with obtaining an acceptable rate of polymerization. Termination of polymerization by radical-radical reaction will lead to chains which contain no active group and therefore cannot be reactivated. The rate of radical-radical termination is proportional to the square of the radical concentration. Furthermore, in the synthesis of block star or branched polymers, chains formed from initiator-derived radicals will constitute a linear homopolymer impurity in the final product. These reaction conditions

therefore require careful choice of the initiator concentration and, where appropriate, the rate of the initiator feed.

It is also desirable to choose other components of the polymerization medium (for example, the solvents, surfactants, additives, and initiator) such that 5 they have a low transfer constant towards the propagating radical. Chain transfer to these species will lead to the formation of chains which do not contain the active group.

As a general guide in choosing conditions for the synthesis of narrow polydispersity polymers, the concentration of initiator(s) and other reaction 10 conditions (solvent(s) if any, reaction temperature, reaction pressure, surfactants if any, other additives) should be chosen such that the molecular weight of polymer formed in the absence of the CTA is at least twice that formed in its presence. In polymerizations where termination is solely by disproportionation, this equates to choosing an initiator concentration such that the total moles of initiating radicals 15 formed during the polymerization is less than 0.5 times that of the total moles of CTA. More preferably, conditions should be chosen such that the molecular weight of polymer formed in the absence of the CTA is at least 5-fold that formed in its presence ( $[\text{initiating radicals}]/[\text{CTA}] < 0.2$ ).

Thus, the polydispersity can be controlled by varying the number of moles 20 of CTA to the number of moles initiating radicals. Lower polydispersities are obtained by increasing this ratio; higher polydispersities are obtained by decreasing this ratio.

With these provisos, the polymerization process according to the present 25 invention is performed under the conditions typical of conventional free-radical polymerization. Polymerization employing the above described CTAs is suitably carried out with temperatures during the reaction in the range -20 to 200°C, preferably in the range 40-160°C.

The process of this invention can be carried out in emulsion, solution or 30 suspension in either a batch, semi-batch, continuous, or feed mode. Otherwise- conventional procedures can be used to produce narrow polydispersity polymers. For lowest polydispersity polymers, the CTA is added before polymerization is commenced. For example, when carried out in batch mode in solution, the reactor is typically charged with CTA and monomer or medium plus monomer. To the mixture is then added the desired amount of initiator and the mixture is heated for 35 a time which is dictated by the desired conversion and molecular weight. Polymers with broad, yet controlled, polydispersity or with multimodal molecular weight distribution can be produced by controlled addition of the CTA over the course of the polymerization process.

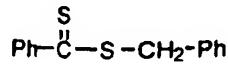
In the case of emulsion or suspension polymerization the medium will often be predominantly water and the conventional stabilizers, dispersants and other additives can be present. For solution polymerization, the reaction medium can be chosen from a wide range of media to suit the monomer(s) being used.

5 As has already been stated, the use of feed polymerization conditions allows the use of CTAs with lower transfer constants and allows the synthesis of block polymers that are not readily achieved using batch polymerization processes. If the polymerization is carried out as a feed system the reaction can be carried out as follows. The reactor is charged with the chosen medium, the CTA 10 and optionally a portion of the monomer(s). Into a separate vessel is placed the remaining monomer(s). Initiator is dissolved or suspended in reaction medium in another separate vessel. The medium in the reactor is heated and stirred while the monomer + medium and initiator + medium are introduced, for example by a syringe pump or other pumping device. The rate and duration of feed is 15 determined largely by the quantity of solution, the desired monomer/CTA/initiator ratio and the rate of the polymerization. When the feed is complete, heating can be continued for an additional period.

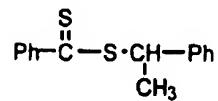
Following completion of the polymerization, the polymer can be isolated by stripping off the medium and unreacted monomer(s) or by precipitation with a 20 non-solvent. Alternatively, the polymer solution/emulsion can be used as such, if appropriate to its application.

25 The invention has wide applicability in the field of free radical polymerization and can be used to produce polymers and compositions for coatings, including clear coats and base coat finishes or paints for automobiles and other vehicles or maintenance finishes for a wide variety of substrates. Such 30 coatings can further include pigments, durability agents, corrosion and oxidation inhibitors, rheology control agents, metallic flakes and other additives. Block and star, and branched polymers can be used as compatibilisers, thermoplastic elastomers, dispersing agents or rheology control agents. Additional applications for polymers of the invention are in the fields of imaging, electronics(e.g., photoresists), engineering plastics, adhesives, sealants, and polymers in general.

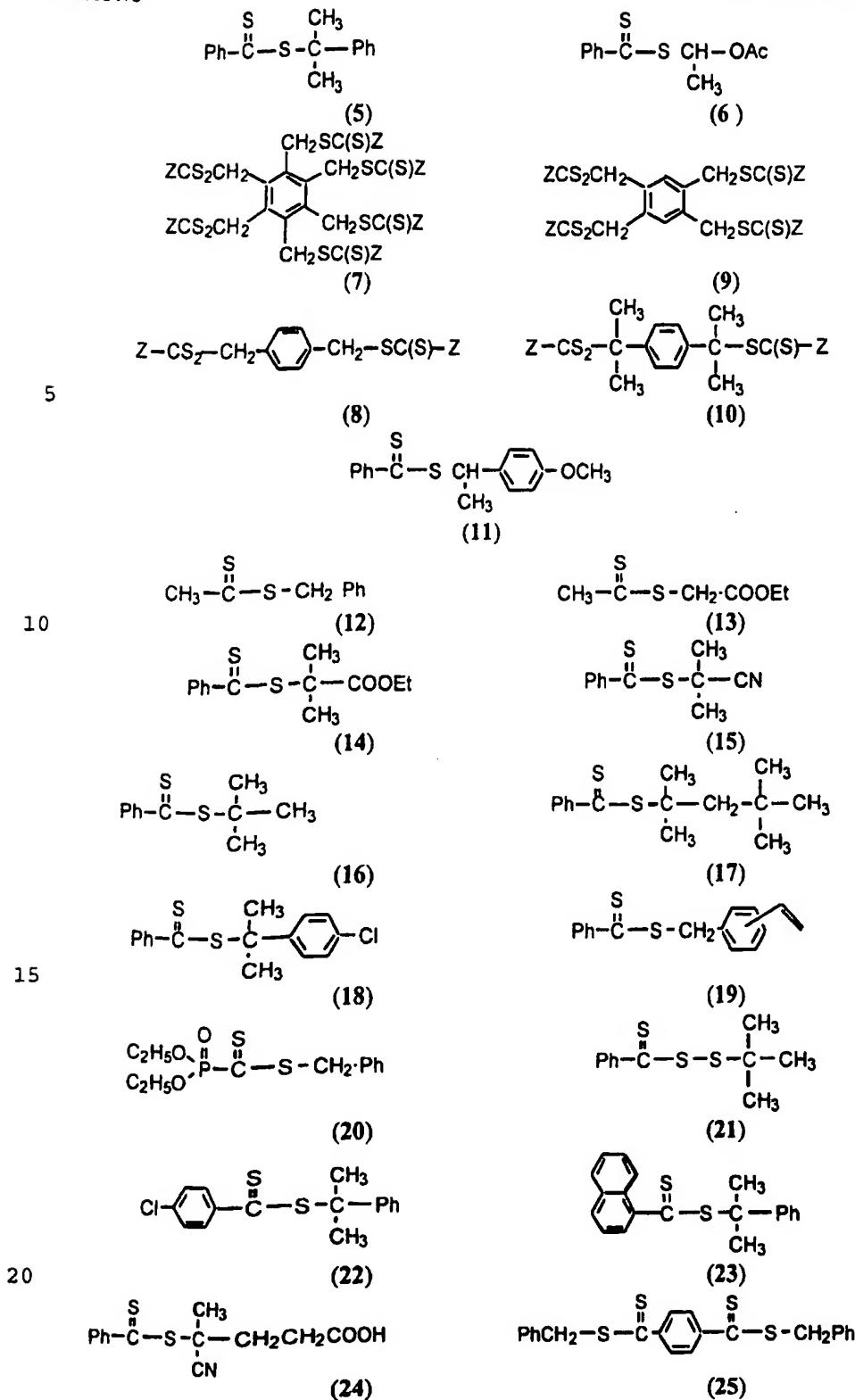
Preferred chain transfer agents applicable in the process of this invention are as follows:

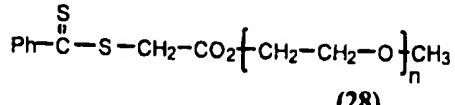
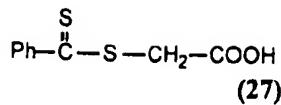
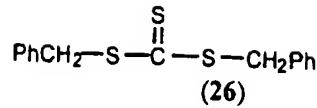


(3)

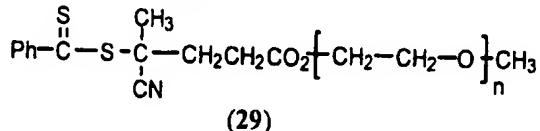


(4)





5 and



wherein Z is phenyl.

10

## EXAMPLES 1 TO 18

### PREPARATION OF THIOCARBONYLTHIO COMPOUNDS

The processes for making compounds (3) to (29) are as follows: Procedures 1-11 describe the preparation of known CTA compounds. Examples 1-18 describe the synthesis of novel CTA compounds.

15

#### Procedure 1

##### Preparation of Dithiobenzoic acid and 4-chlorodithiobenzoic acid

Dithiobenzoic acid and 4-chlorodithiobenzoic acid were prepared according to known procedures. For instance, see the method described in German Patent 1,274,121 (1968); (CA70: 3573v).

20

#### Procedure 2

##### Preparation of benzyl dithiobenzoate (3) (C, p=1, R = $\text{CH}_2\text{Ph}$ , Z = Ph)

This title compound was prepared by a modification of the one-pot procedure described in *Recueil*, 92, 601 (1973). Phenyl magnesium bromide was prepared from bromobenzene (62.8 g) and magnesium turnings (10 g) in dry tetrahydrofuran (300 mL). The solution was warmed to 40 °C and carbon disulfide (30.44 g) was added over 15 minutes whilst maintaining the reaction temperature at 40°C. To the resultant dark brown mixture was added benzyl bromide (76.95 g) over 15 minutes. The reaction temperature was raised to 50 °C and maintained at that temperature for a further 45 minutes. Ice water (1.5L) was added and the organic products extracted with diethyl ether (total 2L). The ethereal phase was washed with water (1L), brine (500 mL) and dried over anhydrous magnesium sulfate. After removal of solvent and vacuum distillation of the residue, benzyl dithiobenzoate (3) was obtained as a red oil (60.2 g, 61.7% yield), b.p. 152 °C (0.02 mmHg) [lit (Beilstein, E III 9, 1998): b.p. 179-180°C at 3 mmHg].  $^1\text{H-nmr}$  ( $\text{CDCl}_3$ ) d (ppm): 4.60 (s, 2H); 7.30-7.60 (m, 8H) and 8.02 (m, 2H).

Procedure 3**Preparation of 1-phenylethyl dithiobenzoate (4) (C, p=1, R = CH(CH<sub>3</sub>)Ph, Z = Ph)**

5 Dithiobenzoic acid (9.9 g), styrene (10 mL) and carbon tetrachloride (30 mL) were combined and the mixture heated at 70 °C for 4 hours. The resultant mixture was reduced to a crude oil. The yield of 1-phenylethyl dithiobenzoate (4) was 43.4% after purification by column chromatography (aluminium oxide (activity III), petroleum spirit 40-60 °C eluent). <sup>1</sup>H-nmr (CDCl<sub>3</sub>) d (ppm): 1.92 (d, 3H); 5.39 (q, 1H); 7.34-7.62 (m, 8H) and 8.08 (m, 2H).

Example 1**Preparation of 2-phenylprop-2-yl dithiobenzoate (5) (C, p=1, R = C(CH<sub>3</sub>)<sub>2</sub>Ph, Z = Ph)**

15 A mixture of dithiobenzoic acid (10.59 g),  $\alpha$ -methylstyrene (10 g) and carbon tetrachloride (40 mL) was heated at 70 °C for 4 hours. The resultant mixture was reduced to a crude oil which was purified by column chromatography (aluminium oxide (activity III), *n*-hexane eluent) to give 2-phenylprop-2-yl dithiobenzoate (5) (6.1 g, 32.6% yield) as a dark purple oil. <sup>1</sup>H-nmr (CDCl<sub>3</sub>) d (ppm): 2.03 (s, 6H); 7.20-7.60 (m, 8H) and 7.86 (m, 2H).

Example 2**Preparation of 1-acetoxyethyl dithiobenzoate (6) (C, p=1, R = CH(CH<sub>3</sub>)OAc; Z = Ph)**

25 A mixture of dithiobenzoic acid (4 g), vinyl acetate (10 mL) and carbon tetrachloride (15 mL) was heated at 70 °C for 16 hours. The resultant mixture was reduced and the residue purified by column chromatography (aluminium oxide column (activity III), *n*-hexane eluent) to give 1-acetoxyethyl dithiobenzoate (6) (3.21 g, 51.5% yield) as a dark red oil. <sup>1</sup>H-nmr (CDCl<sub>3</sub>) d (ppm): 1.80 (d, 3H); 2.09 (s, 3H); 6.75 (q, 1H); 7.34-7.60 (m, 3H) and 7.97 (m, 2H).

Example 3**Preparation of hexakis(thiobenzoylthiomethyl)benzene (9, Z=Ph) (C, p=6, R= C<sub>6</sub>(CH<sub>2</sub>)<sub>6</sub>, Z = Ph)**

35 Hexakis(thiobenzoylthiomethyl)benzene was prepared from hexakis(bromomethyl)benzene according to the method described for the preparation of benzyl dithiobenzoate (3) with the modification that the reaction mixture was heated at 50°C for 3 hours. After the usual work-up, recrystallization

from . ' chloroform/ethanol gave the title compound as a red solid (77% yield), m.p. 222-224 °C (dec).  $^1\text{H-nmr}$  ( $\text{CDCl}_3$ ) d (ppm): 4.66 (s, 12H); 7.30-7.60 (m, 18H) and 7.94 (m, 12H).

5

Example 4

**Preparation of 1,4-bis(thiobenzoylthiomethyl)benzene (8, Z=Ph) (C, p=2, R=  $\text{C}_6\text{H}_4(\text{CH}_2)_2$ , Z = Ph)**

1,4-Bis(thiobenzoylthiomethyl)benzene was prepared from a,a'-dibromo-p-xylene according to the method described for the preparation of benzyl dithiobenzoate (3) with the modification that the reaction mixture was heated at 40°C for 1.5 hours. After the usual work-up, recrystallization from ethanol gave the title compound as a red solid (66.7% yield), m.p. 95-97°C.  $^1\text{H-nmr}$  ( $\text{CDCl}_3$ ) d (ppm): 4.60 (s, 4H); 7.34-7.60 (m, 6H) and 8.00 (m, 4H).

15

Example 5

**Preparation of 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene (9) (C, p=4, R=  $\text{C}_6\text{H}_2(\text{CH}_2)_4$ , Z = Ph)**

1,2,4,5-Tetrakis(thiobenzoylthiomethyl)benzene was prepared from 1,2,4,5-tetrakis-(bromomethyl)benzene according to the method described for the preparation of benzyl dithiobenzoate (3) with the modification that the reaction mixture was heated at 40 °C for 1 hour. The usual work-up gave a red solid which was recrystallized from 1:4 benzene/ethanol to give 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene (47% yield), m.p. 142-143.5 °C (dec).  $^1\text{H-nmr}$  ( $\text{CDCl}_3$ ) d (ppm): 4.65 (s, 8H); 7.30-7.58 (m, 14H) and 7.97 (m, 8H).

25

Example 6

**Preparation of 1,4-bis-(2-(thiobenzoylthio)prop-2-yl)benzene (10) (C, p=2, R= 1,4- $\text{C}_6\text{H}_4(\text{CH}_3)_2)_2$ , Z = Ph)**

1,4-diisopropenylbenzene (3.96 g) was added to a solution of dithiobenzoic acid (8 g) in carbon tetrachloride (50 mL) and the mixture heated at 70 °C for 16 hours. Removal of the solvent, followed by trituration with 1:2 diethyl ether/n-hexane allowed isolation of the title compound as a purple solid (2.87 g, 24.6% yield), m.p. 143-145 °C (dec).  $^1\text{H-nmr}$  ( $\text{CDCl}_3$ ) d (ppm): 2.00 (s, 12H); 7.33 (m, 4H); 7.49 (m, 2H); 7.50 (s, 4H) and 7.86 (m, 4H).

Example 7**Preparation of 1-(4-methoxyphenyl)ethyl dithiobenzoate (11) (C, p=1, R=4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)CH; Z = Ph)**

5 A mixture of dithiobenzoic acid (3.6 g), 4-vinylanisole (2.9 g) and carbon tetrachloride (20 mL) were heated at 70 °C overnight. The solvent was evaporated and the residue subjected to column chromatography (aluminium oxide (activity III) column, 2% diethyl ether in *n*-hexane eluent) which gave the title compound (53% yield). <sup>1</sup>H-nmr (CDCl<sub>3</sub>) d (ppm): 1.80 (d, 3H, SCHCH<sub>3</sub>); 3.80 (s, 3H, OCH<sub>3</sub>); 5.22 (q, 1H, SCHCH<sub>3</sub>) and 6.88-7.97 (m, 9H, ArH).

10

Procedure 4**Preparation of benzyl dithioacetate (12) (C, p=1, R = CH<sub>2</sub>Ph; Z = CH<sub>3</sub>)**

Methyl magnesium chloride (10 mL, 3M solution in THF) was diluted with THF (10 mL) and the resulting solution warmed to 40 °C. Carbon disulfide (2.28 g, 0.03 mol) was added over 10 minutes while maintaining the reaction temperature at 40 °C. The reaction was cooled to room temperature before adding benzyl bromide (5.1 g, 0.03 mol) over 15 minutes. The reaction temperature was increased to 50 °C and maintained for a further 45 minutes. Water (100 mL) was added and the organic products extracted with *n*-hexane (3 X 60 mL). The combined organic extracts were washed with water, brine and dried over anhydrous magnesium sulfate. After removal of solvent and column chromatography (Kieselgel-60, 70-230 mesh, 5% diethyl ether in *n*-hexane eluent), pure benzyl dithioacetate was obtained as a golden oil (3 g, 55% yield). <sup>1</sup>H-nmr (CDCl<sub>3</sub>) d(ppm): 2.90 (s, 3H); 4.46 (s, 2H) and 7.31 (m, 5H).

25

Procedure 5**Preparation of ethoxycarbonylmethyl dithioacetate (13) (C, p=1, R = CH<sub>2</sub>COOEt; Z = CH<sub>3</sub>)**

Methyl magnesium chloride (10 mL, 3M solution in THF) was diluted with THF (10 mL) and the resulting solution warmed to 40 °C. Carbon disulfide (2.28 g, 0.03 mol) was added over 10 minutes while maintaining the reaction temperature at 40 °C. The reaction was cooled to room temperature before adding ethyl bromoacetate (5.01 g, 0.03 mol) over 15 minutes. The reaction temperature was increased to 50 °C and maintained for a further 4 hours. Water (100 mL) was added and the organic products were extracted with ethyl acetate (3 X 60 mL). The combined organic extracts were washed with water, brine and dried over anhydrous magnesium sulfate. After removal of solvent and column chromatography (Kieselgel-60, 70-230 mesh, 10% diethyl ether in *n*-hexane eluent), pure ethoxycarbonylmethyl dithioacetate was obtained as a golden oil (1.3

30

35

g, 24.3 % yield).  $^1\text{H-nmr}$  ( $\text{CDCl}_3$ ) d(ppm): 1.25 (t, 3H); 2.90 (s, 3H); 4.07 (s, 2H) and 4.20 (q, 2H).

Example 8

5 **Preparation of 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14) (C, p=1, R =  $\text{C}(\text{CH}_3)_2\text{COOEt}$ ; Z = Ph)**

Phenyl magnesium bromide was prepared from bromobenzene (6.28 g, 0.04 mol) and magnesium turnings (1 g) in dry THF (30 mL). The solution was warmed to 40°C and carbon disulfide (3.05 g, 0.04 mol) was added over 15 minutes while maintaining the reaction temperature at 40°C. To the resultant dark brown solution was added ethyl  $\alpha$ -bromo isobutyrate (7 g, 0.036 mol). The reaction temperature was raised to 80°C and maintained for 60 hours. Ice water (50 mL) was added and the organic products were extracted with diethyl ether (3 X 50 mL). The combined organic extracts were washed with water, brine and dried over anhydrous magnesium sulfate. After removal of solvent and purification by column chromatography (Kieselgel-60, 70-230 mesh, *n*-hexane/diethyl ether (9:1) eluent), 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate was obtained as a red oil (4.52 g, 42.2% yield).  $^1\text{H-nmr}$  ( $\text{CDCl}_3$ ) d (ppm): 1.25 (t, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.77 (s, 6H, 2x $\text{CH}_3$ ), 4.17 (q, 2H,  $\text{OCH}_2\text{CH}_3$ ), 7.35 (dd, 2H, meta-ArH), 7.52 (dd, 1H, para-ArH) and 7.95 (d, 2H, ortho-ArH).

Example 9

**Preparation of 2-cyanoprop-2-yl dithiobenzoate (15) (C, p=1, R =  $\text{C}(\text{CH}_3)_2\text{CN}$ ; Z = Ph)**

25 2-Bromo-2-cyanopropane was prepared by the procedure of Chrzaszczewska and Popiel (*Roczniki Chem.*, 7, 74-8 (1927); *Chem. Abstr.*, (1928) 22:13436). 2-Cyanoprop-2-yl dithiobenzoate (15) was prepared from 2-bromo-2-cyanopropane by a method similar to that used to prepare compound (14) with the modification that the reaction was maintained at 50°C for 24 hours.

30 After work-up and purification (column chromatography on Kieselgel-60, 70-230 mesh, *n*-hexane/diethyl ether 9:1 eluent), 2-cyanoprop-2-yl dithiobenzoate (15) was obtained as a dark red oil (1.9 g, 43% yield).  $^1\text{H-nmr}$  ( $\text{CDCl}_3$ ) d (ppm): 1.95 (s, 6H, 2x $\text{CH}_3$ ), 7.38 (dd, 2H, meta-ArH), 7.57 (dd, 1H, para-ArH) and 7.92 (d, 2H, ortho-ArH).  $^{13}\text{C-nmr}$  ( $\text{CDCl}_3$ ) d (ppm): 26.5, 41.7, 120.0 (CN), 126.6, 128.5, 132.9, 144.5 and 227.

Procedure 6

**Preparation of *tert*-butyl dithiobenzoate (16) (C, p=1, R =  $\text{C}(\text{CH}_3)_3$ ; Z = Ph)**

The synthesis of *t*-butyl dithiobenzoate (16) was carried out in two steps.

i) S-*t*-butyl thiobenzoate *t*-Butyl mercaptu. (6.15 g, 0.068 mol) was added dropwise to a solution of benzoyl chloride (10.5 g, 0.075 mol) in pyridine (6 g).

The resulting mixture was allowed to stir for two hours at room temperature then poured onto ice-water and the mixture extracted with diethyl ether. The organic

5 extract was washed with dilute HCl, water and brine and finally dried over anhydrous sodium sulfate. After removal of solvent and vacuum distillation, S-*t*-butyl thiobenzoate was obtained (6.64 g, 50.1% yield), b.p. 86°C (0.8 mmHg).

<sup>1</sup>H-nmr (CDCl<sub>3</sub>) d (ppm): 1.60 (s, 9H, 3xCH<sub>3</sub>), 7.41 (m, 2H, ArH), 7.54 (m, 1H, ArH) and 7.94 (d, 2H, ArH). <sup>13</sup>C-nmr (CDCl<sub>3</sub>) d (ppm): 29.8, 48.0, 126.8,

10 128.3, 132.7, 138.6 and 192.9.

ii) *t*-Butyl Dithiobenzoate

A mixture of S-*t*-butyl thiobenzoate (1.94 g, 0.01 mol) and Lawesson's reagent (2.43 g, 0.006 mol) in anhydrous toluene (10 mL) was refluxed for 25 hours. After cooling to room temperature, the reaction mixture was concentrated

15 and the residue subjected to column chromatography (Kieselgel-60, 70-230 mesh, petroleum spirit/diethyl ether 19:1) The title compound was obtained as an oil, 1.37g (65.5%). <sup>1</sup>H-nmr (CDCl<sub>3</sub>) d (ppm): 1.69 (s, 9H, 3xCH<sub>3</sub>), 7.36 (m, 2H, meta-ArH), 7.50 (m, 1H, para-ArH) and 7.88 (d, 2H, ortho-ArH).

<sup>13</sup>C-nmr (CDCl<sub>3</sub>) d (ppm): 28.2, 52.2, 126.6, 128.1, 131.7 and 147.0. The signal 20 due to C=S (d > 220.0 ppm) was beyond the frequency range of the spectrum.

#### Example 10

**Preparation of 2,4,4-trimethylpent-2-yl dithiobenzoate (17) (C, p=1, R = C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>; Z = Ph)**

25 A mixture of dithiobenzoic acid (5 g), 2,4,4-trimethylpentene (7.3 g) and carbon tetrachloride (25 mL) was heated at 70 °C for two days. The resultant mixture was reduced to a crude oil. Purification of the residue, by column chromatography (Kieselgel-60, 70-230 mesh, petroleum spirit 40-60°C eluent) gave 2,4,4-trimethylpent-2-yl dithiobenzoate (17) (2.74 g, 31.7% yield) as a dark red oil. <sup>1</sup>H-nmr (CDCl<sub>3</sub>) d (ppm): 1.08 (s, 9H, 3xCH<sub>3</sub>), 1.77 (s, 6H, 2xCH<sub>3</sub>), 2.20 (s, 2H, CH<sub>2</sub>), 7.35 (dd, 2H, meta-ArH), 7.49 (dd, 1H, para-ArH) and 7.85 (d, 2H, ortho-ArH). <sup>13</sup>C-nmr (CDCl<sub>3</sub>) d (ppm): 28.3, 31.5, 32.8, 50.5, 57.7, 126.6, 128.1, 131.5 and 147.9. The signal due to C=S (d > 220.0 ppm) was beyond the frequency range of the spectrum.

Example 11**Preparation of 2-(4-chlorophenyl)prop-2-yl dithiobenzoate (18) (C, p=1, R = 4-ClC<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>C; Z = Ph)**

5 Dithiobenzoic acid (6.3 g) and 4-chloro-a-methylstyrene (6 g) were combined and the mixture heated at 70°C overnight. The residue was subjected to column chromatography (Kieselgel-60, 70-230 mesh, *n*-hexane as eluent) which gave the title compound as a purple solid (34.2% yield) m.p. 77-78°C. <sup>1</sup>H-nmr (CDCl<sub>3</sub>) d (ppm): 1.97 (s, 6H, 2xCH<sub>3</sub>), 7.20-7.52 (m, 7H, ArH) and 7.86 (d, 2H, ArH). <sup>13</sup>C-nmr (CDCl<sub>3</sub>) d (ppm): 28.4, 55.7, 126.5, 128.1, 131.9, 132.4, 142.8, 146.0. The signal due to C=S (d > 220.0 ppm) was beyond the frequency range of the spectrum.

Example 12**Preparation of 3- & 4-vinylbenzyl dithiobenzoates (19) (C, p=1, R = CH<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>; Z = Ph)**

15 A mixture of 3- & 4-vinylbenzyl dithiobenzoate (19) was synthesized from a mixture of 3- & 4-(chloromethyl)styrene by a procedure similar to that used for compound (14). The reaction was maintained at 50°C for 24 hours. After work-up and column chromatography (aluminium oxide (activity II-III), *n*-hexane/diethyl ether 49:1 eluent) the mixture of 3- & 4-vinylbenzyl dithiobenzoate (19) was obtained in 42% yield as a red oil. <sup>1</sup>H-nmr (CDCl<sub>3</sub>) d (ppm): 4.60 (s, 2H, CH<sub>2</sub>), 5.28 (d, 1H, CH<sub>2</sub>=CH), 5.77 (d, 1H, CH<sub>2</sub>=CH), 6.72 (dd, 1H, CH<sub>2</sub>=CH), 7.20-7.60 (m, 7H, ArH) and 8.00 (d, 2H, ArH).

Procedure 7**Preparation of S-benzyl diethoxyphosphinyldithioformate (20) (C, p=1, R = CH<sub>2</sub>Ph; Z = (EtO)<sub>2</sub>P(O))**

The title compound (20) was prepared by adapting the procedure described by Grisley, *J. Org. Chem.*, 26, 2544 (1961).

20 To a stirred slurry of sodium hydride (60% dispersion in mineral oil) (8 g, 0.2 mol) in tetrahydrofuran (200 mL) was added diethyl phosphite (27.5 g, 0.2 mol) dropwise under nitrogen. The mixture was stirred until hydrogen evolution ceased (about 15 minutes). The mixture was allowed to cool in an ice-water bath and carbon disulfide (76 g, 1 mol) was added over 15 minutes followed by benzyl chloride (25.2 g, 0.2 mol) in THF (100 mL) over 20 minutes. The resultant mixture was stirred at room temperature for 24 hours. Diethyl ether (200 mL) was added and the mixture washed with water (3x200 mL). The organic layer was dried (MgSO<sub>4</sub>), filtered and evaporated *in vacuo*. After column chromatography

(Kieselgel-60, 70-230 mesh, 1:4 ethyl acetate/*n*-hexane eluent), *tert*-benzyl diethoxyphosphinyldithioformate (20) was obtained (11 g, 18% yield) as a red oil.  $^1\text{H-nmr}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm) 1.43 (t, 6H); 4.38 (s, 2H), 4.65 (q, 4H) and 7.30-7.45 (m, 5H).

5

Procedure 8**Preparation of *tert*-butyl trithioperbenzoate (21) (C, p=1; R =  $(\text{CH}_3)_3\text{CS}$ ; Z = Ph)**

The title compound (21) was prepared according to the procedure described by Aycock and Jurch, *J. Org. Chem.*, 44, 569-572, (1979). The residue was subjected to column chromatography (Kieselgel-60, 70-230 mesh, *n*-hexane eluent) to give the product, *tert*-butyl trithioperbenzoate (21) as a dark purple oil in 60 % yield.  $^1\text{H-nmr}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm) 1.32 (s, 9H), 7.45 (m, 3H) and 8.00 (m, 2H).

Example 13**15 Preparation of 2-phenylprop-2-yl 4-chlorodithiobenzoate (22) (C, p=1, R =  $\text{C}(\text{CH}_3)_2\text{Ph}$ ; Z = *p*-ClC<sub>6</sub>H<sub>4</sub>)**

A mixture of 4-chlorodithiobenzoic acid (13 g) and  $\alpha$ -methylstyrene (15 mL) were heated at 70°C for 1 hour. To the reaction mixture was added *n*-hexane (30 mL) and heating was continued at 70°C for 16 hours. The resultant mixture was reduced to a crude oil. Purification, of the oil by chromatography (aluminium oxide column (activity II-III) *n*-hexane eluent) gave the title compound (22) as a purple oil (8.5 g, 40 %).  $^1\text{H-nmr}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm) 2.00 (s, 6H); 7.30 (m, 5H); 7.55 (d, 2H) and 7.83 (d, 2H).

25

Example 14**Preparation of 2-phenylprop-2-yl 1-dithionaphthalate (23) (C, p=1, R =  $\text{C}(\text{CH}_3)_2\text{Ph}$ ; Z = 1-naphthyl)**

The procedure was analogous to that used for the preparation of compound (5). The reaction of 1-(chloromethyl)naphthalene (17.6 g, 0.1 mol), sulfur (6.4 g, 0.2 mol) and sodium methoxide (25% solution in methanol, 46 mL) in methanol (50 mL) gave 1-dithionaphthoic acid (10 g, 49%). A mixture of 1-dithionaphthoic acid (10 g) and  $\alpha$ -methylstyrene (10 mL) in carbon tetrachloride (20 mL) was heated at 70 °C for 16 hours. After removal of carbon tetrachloride and unreacted  $\alpha$ -methylstyrene, the residue was chromatographed (Kieselgel-60, 70-230 mesh, 5% diethyl ether in *n*-hexane eluent) to yield 2-phenylprop-2-yl 1-dithionaphthalate (23) (9.2 g, 58 %) as a dark red oil.  $^1\text{H-nmr}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm) 2.06 (s, 6H); 7.29-7.55 (m, 7H); 7.66 (m, 2H); 7.85 (m, 2H) and 8.00 (m, 1H).

Example 15

**Preparation of 4-cyanopentanoic acid dithiobenzoate (24) (C, p=1, R = C(CH<sub>3</sub>)(CN)(CH<sub>2</sub>)<sub>3</sub>CO<sub>2</sub>H; Z = Ph)**

Compound (24) can be made by a procedure analogous to that used for  
 5 preparation of compounds (14) and (15). m.p. 97-99°C. <sup>1</sup>H-nmr(CDCl<sub>3</sub>) δ (ppm) 1.95 (s, 3H); 2.40-2.80 (m, 4H); 7.42 (m, 2H); 7.60 (m, 1H) and 7.91 (m, 2H).

Example 16

**Preparation of dibenzyl tetrathioterephthalate (25) (D, m = 2, R = CH<sub>2</sub>Ph; Z' = 1,4-phenylene)**

The sodium salt of tetrathioterephthalic acid was obtained from the reaction of a, a'-dibromo-*p*-xylene (6.6 g, 25 mmol), elemental sulfur (3.2 g, 0.1 mol), and sodium methoxide (25% in methanol, 24 mL, 0.1 mol) in methanol (30 mL) at 70 °C for 5 hours. The reaction mixture was evaporated to dryness and  
 15 then dissolved in acetonitrile (50 mL). This was treated with benzyl chloride (6.3 g, 50 mmol) at room temperature for 16 hours. The suspension was filtered, the solid collected and extracted with chloroform/water. The organic extract was dried and reduced to give the title compound as a red solid (2.14 g, 21%). Melting point: 111-116 °C (dec.). <sup>1</sup>H-nmr (CDCl<sub>3</sub>) δ (ppm) 4.60 (s, 4H), 7.30-7.45 (m, 10H) and 7.97 (s, 4H).

Procedure 10

**Preparation of dibenzyl trithiocarbonate (26) (C, p=1, R = CH<sub>2</sub>Ph; Z = SCH<sub>2</sub>Ph)**

The title compound was prepared according to the procedure described by  
 25 Leung, M-K., et al, *J.Chem.Research (S)*, 478-479, (1995).

Procedure 11

**Preparation of carboxymethyl dithiobenzoate (27) (C, p=1, R = CH<sub>2</sub>COOH; Z = Ph)**

The title compound was prepared according to the procedure of Jensen and  
 30 Pedersen, *Acta Chem. Scand.*, **15**, 1087-1096 (1961). <sup>1</sup>H-nmr (CDCl<sub>3</sub>) δ (ppm) 4.24 (s, 2H), 7.43-8.00 (m, 5H) and 8.33 (s, 1H).

Example 17

**Preparation of poly(ethylene oxide) with dithiobenzoate end group (28) (C, p=1, R = CH<sub>2</sub>COO-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>Me; Z = Ph)**

A mixture of carboxymethyl dithiobenzoate (27) (0.5 g, 2.36 mmol), polyethylene glycol monomethyl ether (MWt. 750) (1.7 g, 2.36 mmol), anhydrous pyridine (2 mL), dicyclohexylcarbodiimide (1.46 g, 7.1 mmol) and 4-

toluenesulfonic acid (10 mg) was stirred under nitrogen at 50 °C for 16 hours. The mixture was reduced *in vacuo* and the residue partitioned between chloroform (10 mL) and saturated aqueous sodium bicarbonate (2 mL). The organic phase was dried over anhydrous sodium sulfate and reduced to a red oil (quantitative yield based on 24).  $^1\text{H-nmr}$  ( $\text{CDCl}_3$ ) d (ppm) 3.35 (s, 3H), 3.53 (br.t, 2H), 3.65 (s, 50H), 3.7 (br.t, 2H), 4.23 (s, 2H), 4.30 (br.t, 2H), 7.38 (t, 2H), 7.54 (t, 1H), 8.0 (d, 2H).

#### Example 18

10 **Preparation of poly(ethylene oxide) with dithiobenzoate end group (29) (C, p=1, R =  $\text{C}(\text{CH}_3)(\text{CN})\text{CH}_2\text{CH}_2\text{COO}-(\text{CH}_2\text{CH}_2\text{O})_n\text{Me}$  ; Z = Ph)**

A mixture of 4-cyano-4-(thiobenzoylthio)pentanoic acid (24) (0.23 g), polyethylene glycol monomethyl ether (1.8 g, MWt 750) and a catalytic amount of 4-(*N,N*-dimethylamino)pyridine in dichloromethane (5 mL) was added by a 15 solution of dicyclohexylcarbodiimide (0.34 g) in dichloromethane (5 mL) at room temperature under nitrogen. The mixture was stirred for two hours and filtered to remove the dicyclohexylurea by-product. The filtrate was extracted with water seven times ( $7 \times 10$  mL), dried over anhydrous magnesium sulfate and reduced to a red waxy solid (quantitative yield based on 24).  $^1\text{H-nmr}$  ( $\text{CDCl}_3$ ) d (ppm) 1.92 20 (s, 3H), 2.60-2.72 (m, 4H), 3.35 (s, 3H), 3.53 (m, 2H), 3.63 (s, 64H), 3.65 (m, 2H), 4.26 (t, 2H), 7.40 (t, 2H), 7.57 (t, 1H) and 7.91 (d, 2H).

25 **The following Examples 19-88 represent non-limiting examples which demonstrate the operation of the process and the products obtainable thereby.**

#### Examples 19 to 88

##### **General Experimental Conditions.**

In all instances, monomers were purified (to remove inhibitors) and flash-distilled immediately prior to use. The experiments referred to as controls were experiments run without the CTA unless otherwise specified. For polymerizations performed in ampoules, degassing was accomplished by repeated freeze-evacuate-thaw cycles. Once degassing was complete, the ampoules were flame sealed under vacuum and completely submerged in an oil bath at the specified 35 temperature for the specified times. The percentage conversions were calculated gravimetrically unless otherwise indicated.

The structures of polymers and block copolymers have been verified by application of appropriate chromatographic and spectroscopic methods. Gel

permeation chromatography (GPC) has been used to establish the molecular weight and molecular weight distribution (polydispersity) of the polymers. Unless otherwise specified, a Waters Associates liquid chromatograph equipped with differential refractometer and  $10^6$ ,  $10^5$ ,  $10^4$ ,  $10^3$ , 500 and 100 Å Ultrastryagel 5 columns was used. Tetrahydrofuran (flow rate of 1.0 mL/min) was used as eluent. The molecular weights are provided as polystyrene equivalents. The terms  $M_n$ ,  $M_w$  and  $M_w/M_n$  are used to indicate the number and weight average molecular weights and the polydispersity respectively. Theoretical molecular weights [ $M_n$  (calc)] were calculated according to the following expression:

10  $M_n$  (calc) = [monomer]/[CTA] x conversion x MWt of monomer  
 For low molecular weight polymers (degree of polymerization < 50), the end group [ZC(=S)S-] can be determined by  $^1\text{H}$  NMR spectroscopy. In cases where the end group is (Aryl)C(=S)S- or (Alkyl)C(=S)S- the end groups can be observed in polymers with degree of polymerization  $\geq 1000$  by UV-Visible  
 15 spectrophotometry. Gel permeation chromatography coupled with UV-Visible spectrophotometry enables a measurement of the purity of block copolymers in these cases.

Example 19

20 **Preparation of low polydispersity poly(methyl methacrylate) using 2-phenylprop-2-yl dithiobenzoate (5)**  
 A stock solution containing methyl methacrylate (15 mL), azobisisobutyronitrile (20 mg) and 2-phenylprop-2-yl dithiobenzoate (5) (60.7 mg) in benzene (5 mL) was prepared. Aliquots (4 mL) were transferred to  
 25 ampoules, degassed and sealed. The ampoules were heated at 60 °C for the times indicated in the Table.

**Table 1: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 60°C**

Entry	time/hr	$M_n$	$M_w/M_n$	% Conv.	$M_n$ (calc)
1	2	9 800	1.27	13.5	8 410
2	4	18 000	1.19	27.3	17 000
3	8	29 800	1.15	51.5	32 100
4	16	56 200	1.12	95.0	59 200

Example 20**Preparation of low polydispersity poly(methyl acrylate) with 1-phenylethyl dithiobenzoate (4)**

Stock solutions (I) of azobisisobutyronitrile (6.6 mg) in benzene (50 mL) and (II) of 1-phenylethyl dithiobenzoate (4) (87.6 mg) in benzene (50 mL) were prepared. Aliquots of stock solution (I) (2 mL) and stock solution (II) (6 mL) were transferred to ampoules containing methyl acrylate (2 mL) which were degassed, sealed and heated at 60 °C for the times specified in Table 2 below.

Table 2: Molecular weight and conversion data for poly(methyl acrylate) prepared with 1-phenylethyl dithiobenzoate (4) at 60°C

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv.
1	20	13 500	1.11	26.2
2	64	28 800	1.13	52.9
3	110	32 700	1.16	63.8

Example 21**Preparation of low polydispersity poly(*n*-butyl acrylate) with 1-phenylethyl dithiobenzoate (4)**

A stock solution (I) of azobisisobutyronitrile (13.4 mg) in benzene (50 mL) and a stock solution (II) of 1-phenylethyl dithiobenzoate (4) (50.6 mg) in benzene (50 mL) were prepared. Aliquots of solution (I) (10 mL) and solution (II) (20 mL) were added to a reaction vessel containing *n*-butyl acrylate (20mL). The reaction mixture was degassed, sealed and heated at 60°C for 2 hours, to give poly(*n*-butyl acrylate) (2.48 g, 13.9% conversion) with M<sub>n</sub> 33,600, M<sub>w</sub> 37,800 and M<sub>w</sub>/M<sub>n</sub> 1.13.

Example 22**Preparation of low polydispersity poly(acrylic acid) using 1-phenylethyl dithiobenzoate (4)**

Stock solution (I) of azobisisobutyronitrile (6.64 mg) in N,N-dimethylformamide (DMF) (25 mL) and stock solution (II) of 1-phenylethyl dithiobenzoate (4) (17.7 mg) in DMF (25 mL) were prepared. Aliquots of stock solution (I) (2 mL), stock solution (II) (6 mL) and acrylic acid (2 mL) were placed in a reaction vessel. The reaction mixture was degassed, sealed and heated at 60°C for 4 hours. After removal of the solvent and excess monomer, poly(acrylic acid) (0.37 g, 17.5% conversion) was obtained. A portion was methylated (tetramethylammonium hydroxide (25% in methanol) and excess methyl iodide) to give poly(methyl acrylate) of M<sub>n</sub> 13792, M<sub>w</sub> 16964 and M<sub>w</sub>/M<sub>n</sub> 1.23.

Example 23**Preparation of low polydispersity polystyrene via bulk polymerization of styrene with benzyl dithiobenzoate (3)**

5 A stock solution of styrene (60 mL) and azobisisobutyronitrile (16.9 mg) was prepared. Aliquots (5 mL) were removed and transferred to ampoules containing benzyl dithiobenzoate (11.4 mg). The ampoules were degassed, sealed and heated at 60°C for the periods of time indicated in the Table below. The results are listed in Table 3 below.

10 **Table 3: Molecular weight and conversion data for polystyrene prepared with benzyl dithiobenzoate at 60°C**

Entry	time /hr	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv.
1 (control)	1	164 000	1.83	1.61
2	1	1 500	1.36	0.68
3	2	2 260	1.27	1.49
4	4	3 630	1.24	3.46
5	8	6 020	1.21	6.92
6	12	8 900	1.16	10.60
7	16	11 780	1.16	13.66
8	20	14 380	1.13	17.16
9	30	18 500	1.12	22.43
10	50	25 200	1.17	31.82
11	100	33 400	1.13	42.32

Example 24**Preparation of low polydispersity polystyrene via bulk polymerization of styrene using 2-phenylprop-2-yl dithiobenzoate (5)**

15 Polystyrene was prepared under the conditions used for Example 5 with 2-phenylprop-2-yl dithiobenzoate (5) (11.4 mg per ampoule) in place of benzyl dithiobenzoate. Results are shown in Table 4 below.

**Table 4: Molecular weight and conversion data for polystyrene prepared with 2-phenylprop-2-yl dithiobenzoate at 60°C**

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv.
1 (control)	1	285 000	1.63	1.67
2	1	833	1.12	0.49
3	4	4 510	1.09	3.74
4	20	21 500	1.14	19.45
5	50	40 000	1.17	37.49
6	100	52 000	1.18	57.33

**Example 25**

**5 Preparation of low polydispersity polystyrene via thermal polymerization of styrene using 1-phenylethyl dithiobenzoate (4) at 100°C**

A stock solution of styrene (10 mL) and 1-phenylethyl dithiobenzoate (4) (24.8 mg) was prepared. Aliquots (2 mL) of this solution were transferred to ampoules which were degassed, sealed and heated at 100 °C for the times indicated in Table 5 below and analyzed by GPC.

**Table 5: Molecular weight and conversion data for polystyrene prepared with 1-phenylethyl dithiobenzoate (4) at 100°C**

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv.
1 (Control)	6	227 000	434 000	1.91	21.7
2	6	5 800	6 300	1.09	9.7
3	20	22 000	25 000	1.15	36.8
4	64	38 500	47 000	1.22	70.6
5	120	50 000	61 000	1.23	91.9

**Example 26**

**15 Preparation of low polydispersity polystyrene via thermal polymerization of styrene using 1-phenylethyl dithiobenzoate (4) at 100°C**

Example 25 was repeated with a threefold higher concentration of 1-phenylethyl dithiobenzoate (4) (75.6 mg) in the stock solution. The results are summarized in the Table 6 below.

**Table 6: Molecular weight and conversion data for polystyrene prepared with 1-phenylethyl dithiobenzoate (4) at 100°C**

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv.
1	6	3 440	37 30	1.08	12.3
2	20	10 000	11 000	1.08	35.0
3	64.5	22 000	24 000	1.10	65.6
4	120	27 000	31 000	1.16	87.6

5

Example 27

**Preparation of low polydispersity polystyrene via thermal polymerizations of styrene using 2-phenylprop-2-yl dithiobenzoate (5) at 100°C**

Example 26 was repeated with 2-phenylprop-2-yl dithiobenzoate (5) in place of 1-phenylethyl dithiobenzoate (4) (same molar concentration). The results 10 are listed in Table 7.

**Table 7: Molecular weight and conversion data for polystyrene prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 100°C**

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv.
1	2	1 520	1 690	1.12	4.3
2	6	5 680	6 140	1.08	14.3
3	20	13 800	14 900	1.08	39.9
4	64	25 000	28 100	1.12	81.0
5	119	26 000	30 000	1.14	88.0

15

Example 28

**Preparation of low polydispersity polystyrene via emulsion polymerization of styrene using benzyl dithiobenzoate (3) at 80°C**

A 5-neck reaction vessel fitted with a stirrer, condenser and thermocouple was charged with water (75 g) and sodium dodecyl sulfate (5 g of 10% aqueous 20 solution). The mixture was degassed under nitrogen at 80°C for 40 minutes. A solution of 4,4'-azobis(4-cyanopentanoic acid) (0.14 g) and benzyl dithiobenzoate (3) (0.215 g) in styrene (3.7 g) was added as a single shot. Further 4,4'-azobis(4-cyanopentanoic acid) (0.209 g) in sodium dodecyl sulfate (1% aq solution) (24 g) at a rate of 0.089mL/min along with styrene (32.9 g) at a rate of 0.2mL/min were 25 added by syringe pumps. On completion of the initiator feed, the reaction was

held at 80 °C for a further 90 minutes. The isolated polystyrene had  $M_n$  53 200;  $M_w/M_n$  1.37 at 73% conversion.

Example 29

5 **Preparation of low polydispersity polystyrene via emulsion polymerizations of styrene using benzyl dithiobenzoate (3) at 80°C**

Example 28 was repeated with a higher concentration of benzyl dithiobenzoate (3) (0.854 g).

The isolated polystyrene had  $M_n$  3 010;  $M_w/M_n$  1.20 at 19% conversion.

10

Example 30

**Preparation of low polydispersity poly(methyl acrylate-*block*-ethyl acrylate)**

A sample of poly(methyl acrylate) (0.17 g,  $M_n$  24 070,  $M_w/M_n$  1.07) made with 1-phenylethyl dithiobenzoate (4) (as described in Example 20) was 15 dissolved in ethyl acrylate (2 mL) and benzene (8 mL) containing azobisisobutyronitrile (0.52 mg). The vessel was degassed, sealed and heated at 60°C for 2 hours to give poly(methyl acrylate-*block*-ethyl acrylate) (0.22 g, 10.8% conversion),  $M_n$  30 900,  $M_w/M_n$  1.10.

20

Example 31

**Preparation of low polydispersity poly(*n*-butyl acrylate-*block*-acrylic acid)**

A stock solution of azobisisobutyronitrile (6.64 mg) in DMF (25 mL) was prepared. In an ampoule, poly(*n*-butyl acrylate) from Example 21, (0.5 g,  $M_n$  33 569,  $M_w/M_n$  1.13) was dissolved in DMF (5.5 mL), acrylic acid (4 mL) and 25 stock solution (0.5 mL). The mixture was degassed, sealed and heated at 60 °C for 2 hours. After removal of the solvent and unreacted monomer, poly(*n*-butyl acrylate-*block*-acrylic acid) was obtained (0.848 g, 8.3% conversion). GPC results (after methylation of the acrylic acid of the diblock):  $M_n$  52 427;  $M_w$  63 342;  $M_w/M_n$  1.19.

30

Example 32

**Preparation of low polydispersity polystyrene using benzyl dithioacetate (12)**

A stock solution of styrene (10 mL), benzyl dithioacetate (12) (17 mg) and azobisisobutyronitrile (2.8 mg) was prepared. Aliquots (2 mL) were removed and 35 transferred to ampoules. The ampoules were degassed, sealed and heated at 60°C for the periods of time indicated in Table 8 below.

**Table 8: Molecular weight and conversion data for polystyrene prepared with benzyl dithioacetate(12) at 60°C**

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv.
1	2	6 840	11 800	1.72	1.8
2	4	8 570	13 500	1.58	5.0
3	16	19 000	25 000	1.32	16.5
4	40	30 000	37 000	1.24	28.9

Example 33

5 **Preparation of low polydispersity poly(*n*-butyl acrylate) using benzyl dithiobenzoate (3)**

Stock solution (I) of azobisisobutyronitrile (13.4 mg) in benzene (50 mL) and stock solution (II) of benzyl dithiobenzoate (3) (9.62 mg) in benzene (10 mL) were prepared.

10 Aliquots of stock solution (I) (2 mL) and stock solution (II) (4 mL) were transferred to ampoules already containing *n*-butyl acrylate (4 mL). The ampoules were degassed, sealed and heated at 60°C for the periods of time indicated in Table 9 below.

15 **Table 9: Molecular weight and conversion data for poly(*n*-butyl acrylate) prepared with benzyl dithiobenzoate (3) at 60°C**

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	M <sub>n</sub> (calc)	% Conv.
1	2	26 000	1.12	25 866	11.4
2	8	92 000	1.14	90 760	40.0

Example 34

20 **Preparation of low polydispersity poly(N,N-dimethyl acrylamide) using benzyl dithiobenzoate(3)**

A stock solution (I) of azobisisobutyronitrile (2.5 mg) and N,N-dimethylacrylamide (10 mL) in benzene (50 mL) was prepared. Stock solution (II) containing benzyl dithiobenzoate (3) (4 mg) in stock solution (I) (20 mL) was prepared. Aliquots of stock solutions (I) and (II) were transferred to ampoules (in the quantities indicated in the Table below). The ampoules were degassed, sealed and heated at 60°C for 1 hour. The molecular weight and polydispersity data are summarised in Table 10 below.

**Table 10: Molecular weight and conversion data for poly(*N,N*-dimethyl acrylamide) prepared with benzyl dithiobenzoate (3) at 60°C**

Entry	Solution (I) (mL)	Solution (II) (mL)	CTA (mg)	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	M <sub>n</sub> (calc)	% Conv.
1	0	10	2	35 000	1.14	30 266	12.9
2	5	5	1	135 000	1.23	120 597	25.7
3	7.5	2.5	0.5	224 000	1.44	293 742	31.3
4 (control)	10	0	0	833 000	2.59	-	76.9

Example 35

5 **Emulsion polymerization of styrene in the presence of benzyl dithioacetate at 80°C with sodium dodecyl sulfate as surfactant and 4,4'-azobis(4-cyanopentanoic acid) as initiator**

A 5-neck reaction vessel fitted with a stirrer, condenser and thermocouple was charged with water (75 g) and sodium dodecyl sulfate (5 g of 10% aqueous

10 solution). The mixture was degassed under nitrogen at 80°C for 40 minutes.

A solution of 4,4'-azobis(4-cyanopentanoic acid) (0.14 g) and benzyl dithioacetate (0.155 g) in styrene (3.7 g) was added as a single shot. Further 4,4'-azobis(4-cyanopentanoic acid) (0.211 g) in sodium dodecyl sulfate (1% aq solution) (24 g) was added at a rate of 0.089 mL/min along with styrene (32.9 g) at a rate of

15 0.2mL/min.

On completion of the initiator feed, the reaction was held at 80°C for a further 90 minutes. The results of the experiment are summarized in Table 11.

**Table 11: Molecular weight and conversion data for polystyrene prepared**

20 **with benzyl dithioacetate in emulsion at 80°C**

Entry	Reaction time /min	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conversion <sup>a</sup>
1	75	21 000	1.27	97 <sup>a</sup>
2	120	29 000	1.26	98 <sup>a</sup>
3	180	35 000	1.33	>99
4	240	37 000	1.35	>99
5	270	38 000	1.34	>99
6	360	36 000	1.38	>99

<sup>a</sup> Instantaneous conversion (conversion of monomer added up to time of sampling).

Example 36**Preparation of narrow polydispersity poly(styrene-*block*-*N,N*-dimethylacrylamide)**

The polystyrene ( $M_n$  20300,  $M_w/M_n$  1.15) used in this experiment was 5 prepared by bulk polymerization of styrene (100 mL) at 60°C for 30.5 hours with azobisisobutyronitrile (28.17 mg) as initiator in the presence of benzyl dithiobenzoate (3) (228 mg).

A solution of the above polystyrene (0.2 g), *N,N*-dimethylacrylamide (2 mL), azobisisobutyronitrile (0.5 mg) and benzene (8 mL) was transferred to an 10 ampoule. The resulting mixture was degassed, sealed and heated at 60°C for 1 hour. The volatiles were removed *in vacuo* to give poly(styrene-*block*-dimethylacrylamide) at 0.4 g, 10.4% conversion, with  $M_n$  43 000 and  $M_w/M_n$  1.24.

15

Example 37**Preparation of low polydispersity poly(4-methylstyrene-*block*-styrene)**

A mixture of polystyrene (0.5 g,  $M_n$  20300,  $M_w/M_n$  1.15, prepared as described in Example 36), 4-methylstyrene (2 mL), azobisisobutyronitrile (2.5 mg) and benzene (0.5 mL) were transferred to an ampoule. The resulting mixture 20 was degassed, sealed and heated at 60°C for 3 hours. Volatiles were removed under reduced pressure to give poly(styrene-*block*-4-methylstyrene) (0.81 g, 17.1% conversion,  $M_n$  25 400 and  $M_w/M_n$  1.19).

25

Example 38**Preparation of low polydispersity poly(methyl methacrylate-*block*-styrene)**

Poly(methyl methacrylate) ( $M_n$  17408,  $M_w/M_n$  1.20) was prepared under the conditions described for Example 19 with a reaction time of 4 h. This polymer (1.7 g) was dissolved in ethyl acetate and the solution transferred to an ampoule. The ethyl acetate was removed under reduced pressure and azobisisobutyronitrile 30 (2.82 mg) and styrene (10 mL) were added. The ampoule was degassed, sealed and heated at 60°C for 20 hours. After removal of the unreacted styrene, poly(methyl methacrylate-*block*-styrene) was obtained (3.9 g, 23.5% conversion) with  $M_n$  35 000;  $M_w$  44 000 ;  $M_w/M_n$  1.24.

Example 39**Preparation of low polydispersity poly(*n*-butyl acrylate) via the solution polymerization of *n*-butyl acrylate at 90°C in the presence of 1,4-****5 bis(thiobenzoylthiomethyl)benzene (8)**

A stock solution of 1,1'-azobis(1-cyclohexanecarbonitrile) (8.03 mg) in benzene (10 mL) was prepared. Aliquots (1 mL) of the stock solution were added to ampoules containing *n*-butyl acrylate (4 mL), 1,4-bis(thiobenzoylthiomethyl)benzene (8) (12.7 mg) and benzene (5 mL). The 10 contents of the ampoules were degassed, sealed and heated at 90°C for the times given in Table 12 below.

**Table 12: Molecular weight and conversion data for poly(*n*-butyl acrylate) prepared with 1,4-bis(thiobenzoylthiomethyl)benzene (8) at 90°C**

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	M <sub>n</sub> (calc)	% Conv.
1	1	5 090	1.21	5 079	4.4
2	5	57 000	1.32	65 571	56.8

15

Example 40**Preparation of low polydispersity poly(*n*-butyl acrylate) via the solution polymerization of *n*-butyl acrylate at 90°C in the presence of 1,4-bis(2-thiobenzoylthioprop-2-yl)benzene (10)**

20 Stock solution (I) of 1,1'-azobis(1-cyclohexanecarbonitrile) (10.09 mg) in benzene (25 mL), and stock solution (II) of 1,4-bis(2-thiobenzoylthioprop-2-yl)benzene (10) (175.1 mg) in benzene (25 mL) were prepared. Aliquots of stock solution (I) (2 mL) and stock solution (II) (4 mL) were added to ampoules containing *n*-butyl acrylate (4 mL). The ampoules were degassed, sealed and 25 heated at 90°C for the times shown in Table 13 below.

**Table 13: Molecular weight and conversion data for poly(*n*-butyl acrylate) prepared with 1,4-bis(2-thiobenzoylthioprop-2-yl)benzene (10) at 90°C**

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	M <sub>n</sub> (calc)	% Conv.
1	5	937	1.13	952	1.6
2	16	28 000	1.21 <sup>a</sup>	27 365	46.0
3	42	41 000	1.37 <sup>a</sup>	43 904	73.8

30 a) trimodal molecular weight distribution

Example 41

Preparation of low polydispersity star polystyrene via the thermal polymerization of styrene at 100°C in the presence of 5 hexakis(thiobenzoylthiomethyl)benzene (7)

A stock solution comprising of styrene (10 mL) and hexakis(thiobenzoylthiomethyl)benzene (7) (48.9 mg) was prepared. Aliquots of the stock solution (2 mL) were transferred to ampoules which were degassed, sealed and heated at 100°C for the times given in Table 14 below.

10

**Table 14: Molecular weight and conversion data for star polystyrene prepared with hexakis(thiobenzoylthiomethyl)benzene (7) at 100°C**

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv.
1	6	1 350	1 530	1.13	0.33
2	20	34 100	46 500	1.36	27.5
3	64	80 000	133 000	1.67	72.1

15

Example 42

Preparation of low polydispersity star polystyrene via the thermal polymerization of styrene at 100°C in the presence of 1,2,4,5-tetrakis-(thiobenzoylthiomethyl)benzene (9)

A stock solution of styrene (10 mL) and 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene (9) (54.5 mg) was prepared. Aliquots (2 mL) of the stock solution were transferred to ampoules which were degassed, sealed and heated at 100°C for the times given in the Table below. Polymer was obtained by removal of the volatiles. The results are summarized in Table 15 below.

20

25

**Table 15: Molecular weight and conversion data for star polystyrene prepared with 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene (9) at 100°C**

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	M <sub>n</sub> (calc)	% Conv.
1	6	989	1 100	1.11	-	0.88
2	20	26 000	31 100	1.20	27 257	22.0
3	64	67 500	87 600	1.30	90 814	73.3

Example 43**Preparation of low polydispersity star polystyrene via the thermal polymerization of styrene at 120°C in the presence of 1,2,4,5-tetrakis-(thiobenzoylthiomethyl)benzene (9)**

5 A stock solution of styrene (10 mL) and 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene (9) (54.5 mg) was prepared. Aliquots (2 mL) of the stock solution were transferred to ampoules which were degassed, sealed and then heated at 120°C for the times given below. The polymer was isolated by removal of the volatiles. The results are summarized in Table 16  
 10 below.

**Table 16: Molecular weight and conversion data for star polystyrene prepared with 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene (9) at 120°C**

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	M <sub>n</sub> (calc)	% Conv.
1	6	43 000	55 000	1.29	51416	41.5
2	20	75 000	109 000	1.44	100353	81.0
3	64	80 000	119 000	1.49	109770	88.6

Example 44**Preparation of low polydispersity poly(methyl methacrylate) using 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14)**

15 The method of Example 19 was used with 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14) (same molar concentrations). Results are summarized in  
 20 Table 17 below.

**Table 17: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14) at 60°C**

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv.
1	2	30 000	1.89	22.7
2	4	35 000	1.72	37.1
3	8	40 000	1.66	67.4
4	16	53 000	1.48	>95

Example 45**Preparation of low polydispersity poly(methyl methacrylate) with 2-cyanoprop-2-yl dithiobenzoate (15)**

5 The method of Example 19 was used with 2-cyanoprop-2-yl dithiobenzoate (15) (same molar concentrations). Results are summarized in Table 18 below.

10 **Table 18: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-cyanoprop-2-yl dithiobenzoate (15) at 60°C**

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv.
1	2	9 200	1.26	16.2
2	4	17 000	1.19	39.4
3	8	30 000	1.17	68.6
4	16	52 000	1.16	>90

Example 46**Preparation of low polydispersity poly(methyl methacrylate) using 2-(4-chlorophenyl)prop-2-yl dithiobenzoate (18)**

15 The experimental conditions described in Example 19 (same molar concentrations) were used to prepare low polydispersity poly(methyl methacrylate) with 2-(4-chlorophenyl)prop-2-yl dithiobenzoate (18). Results are summarized in Table 19 below.

20 **Table 19: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-(4-chlorophenyl)propyl dithiobenzoate (18) at 60 °C.**

Entry	time/hr	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	% Conv.	M <sub>n</sub> (calc)
1	2	8 840	1.25	15.1	9 390
2	4	16 200	1.17	31.0	19 330
3	8	30 400	1.13	63.3	39 260
4	16	52 800	1.14	>95	59 205

Example 47

25 **Preparation of low polydispersity poly(methyl methacrylate) with *tert*-butyl trithioperbenzoate (21)**

The experimental conditions described in Example 19 (same molar concentrations) were used to prepare low polydispersity poly(methyl methacrylate) with *tert*-butyl trithioperbenzoate (21). After heating at 60 °C for 16 hours, poly(methyl methacrylate) was obtained (62.8% conversion; Mn 92 5 000;  $M_w/M_n$  1.34).

#### Example 48

##### **Preparation of low polydispersity poly(methyl methacrylate) with 2-phenylprop-2-yl 4-chlorodithiobenzoate (22)**

The experimental conditions described in Example 19 (same molar 10 concentrations) were used to prepare low polydispersity poly(methyl methacrylate) with 2-phenylprop-2-yl 4-chlorodithiobenzoate (22). After heating at 60 °C for 16 hours, poly(methyl methacrylate) was obtained (95 % conversion; Mn 55 000;  $M_w/M_n$  1.07).

#### Example 49

##### **Preparation of low polydispersity poly(methyl methacrylate) with 2-phenylprop-2-yl 1-dithionaphthalate (23)**

The experimental conditions described in Example 19 (same molar 20 concentrations) were used to prepare low polydispersity poly(methyl methacrylate) with 2-phenylprop-2-yl 1-dithionaphthalate (23). After heating at 60 °C for 16 hours, poly(methyl methacrylate) was obtained (95 % conversion; Mn 57500;  $M_w/M_n$  1.10).

#### Example 50

##### **Preparation of low polydispersity poly(methyl methacrylate) in presence of 2-phenylprop-2-yl dithiobenzoate (5) with benzoyl peroxide as initiator**

A stock solution containing methyl methacrylate (20 mL), benzoyl peroxide (24.2 mg) and benzene (5 mL) was prepared. An aliquot (5 mL) of the stock solution was removed and 4mL of this was placed in an ampoule labelled as control run (entry 1). 2-phenylprop-2-yl dithiobenzoate (5) (54.5 mg) was added 30 to the remaining 20 mL of stock solution. Aliquots of this solution (4 mL) were transferred to four ampoules which were degassed, sealed and heated at 60 °C. The results are summarized in Table 20 below.